made by warm-up and methyl bromide added subsequently, there is no exchange reaction. Consequently, it is proposed that in the black matrix the magnesium atoms are weakly bound to the halogen atom of the alkyl halide, thus limiting its movement and self-condensation to make a metal film; magnesium atoms bound in this manner are readily transferred to other alkyl halides, and since methyl halides are more reactive than propyl, the former reacts preferentially.

These solvent-free organomagnesium compounds do not behave like the traditional Grignard reagent prepared in donating solvents. For example, propyl Grignard reagent adds readily to acetone making the tertiary alcohol. Our propylmagnesium compound enolizes acetone. Addition to perdeuterioacetone results in direct formation of monodeuteriopropane, and work-up of the residue yields diacetone alcohol, the aldol product, presumably formed from the magnesioenolate. Also, our methylmagnesium compound reacts with crotonaldehyde by 1,2 addition rather than 1,4.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research (Grant No. 1983) with gratitude.

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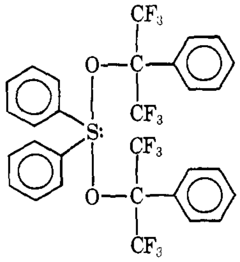
Sulfuranes. VIII. The Isolation and Characterization of a Dialkoxydiarylsulfurane Oxide, a Crystalline, Pentacoordinate Sulfur(VI) Species

Sir:

In preceding publications[1] the isolation and characterization[2] and X-ray crystal structure[1,3] of the diaryldialkoxysulfurane **1** have been reported. This compound can be viewed as the ketal analog of a sulfoxide. We now report the first example of a ketal analog of a sulfone, compound **2**, which we shall call a dialkoxydiarylsulfurane oxide.



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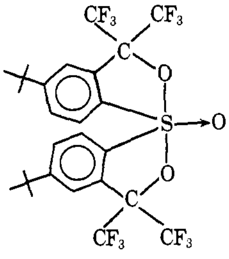
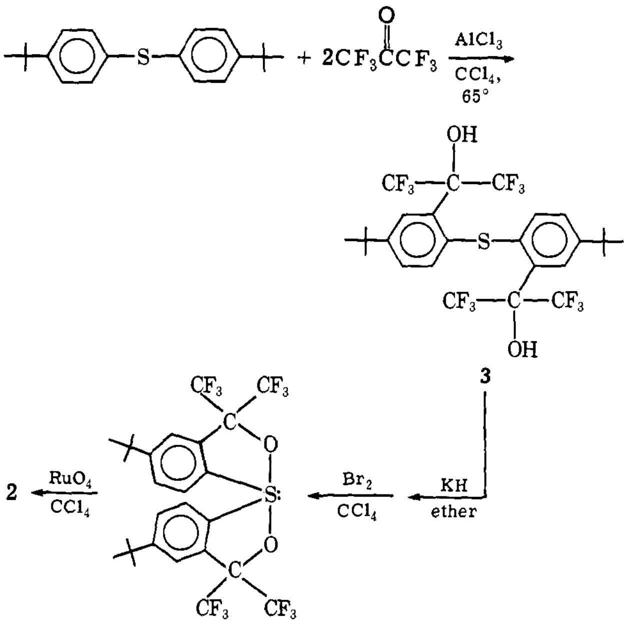


2

Diol **3** was prepared by heating (1 hr at 65°) a sealed tube containing a carbon tetrachloride solution of bis(*p-tert*-butylphenyl) sulfide[4] with excess hexafluoroacetone in the presence of 28 mol % anhydrous aluminum chloride. Compound **3** was obtained by chromatography on alumina in 27% crude yield. Recrystallization from petroleum ether gave white crystals, mp 116.5–119°, identified as **3** by ^{19}F and ^{1}H nmr and mass spectra. (All compounds described in this paper gave satisfactory elemental analyses.)



An ether solution of diol **3** was treated with potassium hydride. The ether was evaporated and the resulting potassium salt was redissolved in carbon tetrachloride. The dialkoxide was then oxidized to sulfurane **4** with 1 equiv of bromine. Upon removal of the precipitated potassium bromide by filtration and removal of the solvent *in vacuo*, an almost quantitative yield of crude sulfurane **4** was obtained. This was recrystallized from petroleum ether to give white prisms, mp 159–160.5°, identified as **4** by ^{19}F and ^{1}H nmr and mass spectra. The ^{19}F nmr spectrum is of particular interest in that the observation of two quartets (J_{FF} = 9 Hz) at 73.9 and 77.1 ppm (upfield from $CFCl_3$) is consistent with the expected[1,2] trigonal-bipyramidal geometry, with apical alkoxy ligands and equatorial aryl ligands on sulfur. This geometry renders the geminal CF_3 groups nonequivalent.

Treatment of sulfurane **4** in carbon tetrachloride with a carbon tetrachloride solution of ruthenium tetroxide afforded a nearly quantitative conversion (by nmr) of **4** to the sulfurane oxide, **2**. Filtration of the precipitated RuO_2 followed by evaporation of the solvent gave 90% of crude **2**. Recrystallization of the solid product from petroleum ether gave white needles, mp 183.5–184°.

Anal. Calcd for $C_{26}H_{24}F_{12}O_3S$: C, 48.45; H, 3.75; S, 4.97. Found: C, 48.72; H, 3.70; S, 5.02.

The mass spectrum (70 eV) showed a small molecular ion at *m/e* 644 (1.53% of base peak). There were also prominent peaks at *m/e* 629 (16.57%, M − CH_3), *m/e* 625 (16.85%, M − F), *m/e* 575 (100%, M − CF_3), *m/e* 565 (11.62%, M − CH_3SO_2), and *m/e* 559 (15.94%, M − CF_3O). High-resolution peak matching techniques show the molecular ion at *m/e* 644.1244 (calcd for **2**, 644.1255). The 100-MHz fluorine-decoupled ^{1}H nmr (CCl_4) shows peaks at δ 8.610 (d, 2, protons ortho to sulfur, J_{AB} = 9.3 Hz), 7.750 (d of d, protons ortho to

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(1) For paper VII in this series see I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **94**, 5010 (1972).

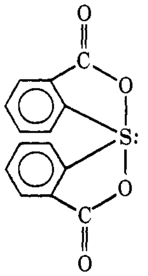
(2) (a) J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2341 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997 (1972).

(3) (a) I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **93**, 6674 (1971).

(4) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

tert-butyl and to other proton, $J_{AB} = 9.2$ Hz, $J_{BC} = 2.0$ Hz), 7.745 (d, br s in absence of decoupling, total area for δ 7.750 and 7.745 = 4, proton ortho to *tert*-butyl and ortho to hexafluorocumyl group, $J_{BC} = 2.0$ Hz), 1.39 (s, 18, *tert*-butyl protons). The ^{19}F nmr shows two quartets at 74.6 and 75.2 ppm upfield from $CFCl_3$ ($J_{FF} \cong 8$ Hz).

In contrast to **1**, which shows great reactivity toward water or alcohols,[2] neither **2** nor **4** is readily hydrolyzed. Sulfurane **4** does not react with *tert*-butyl alcohol at room temperature and is stable to treatment with 9:1 tetrahydrofuran–water heated to reflux, and to hydrochloric acid or sodium hydroxide in the same solvent system when heated to reflux for 2 hr. The low hydrolytic reactivity of **4** is even more pronounced than that reported by Kapovits and Kálmán[5] for sulfurane **5**, which was hydrolyzed to the sulfoxide upon heating for 30 min in 9:1 acetone–water. Attempts to hydrolyze **2** and **4** are currently underway in these laboratories along with further investigations of their chemistry.



5

An analogous oxidation employing ruthenium tetroxide was attempted on the much more sterically hindered compound **1** but no intermediate analogous to **2** could be detected.

The nonequivalence of geminal CF_3 groups seen in the ^{19}F nmr spectrum of **2** is consistent with a trigonal-bipyramidal geometry with apical alkoxy ligands and equatorial aryl and oxide ligands. The only other known[6] example of this sort of pentacoordinate sulfur compound, SOF_4, appears to have such a trigonal-bipyramidal geometry,[7] although there is some uncertainty as to the detailed structure.[8,9]

Acknowledgment. Support for this research was provided by Grant No. GP 30491X and by a departmental equipment grant for the purchase of nmr instrumentation from the National Science Foundation.

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(5) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

(6) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Amer. Chem. Soc.*, **78**, 1553 (1956). Another possible example has been proposed by R. J. Gillespie and J. V. Oubridge, *Proc. Chem. Soc. London*, 308 (1960).

(7) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).

(8) J. L. Hencher, D. W. J. Cruickshank, and S. H. Bauer, *ibid.*, **48**, 518 (1968).

(9) G. Gundersen and K. Hedberg, *ibid.*, **51**, 2500 (1969).

Book Reviews

Organic Peroxides. Volume II. Edited by DANIEL SWERN. Wiley-Interscience, New York, N. Y. 1971. ix + 963 pp. $40.00.

This volume contains articles by eight authors and represents a very comprehensive review of peroxide chemistry covering the literature to 1969. Extensive coverage is given to alkyl hydroperoxides, metal-catalyzed reactions of peroxides, peroxy acids as oxidizing agents, and acyl peroxides. Considerable attention is paid in two articles to physical properties and detection of peroxides.

The text is well laid out with numerous structures, mechanisms, and exemplary tables. It is well documented with nearly 4000 references. The cost of this book, though in line with its size and scope, will dictate its use mainly as a specialized reference.

John T. Groves, *University of Michigan*

Some Modern Methods of Organic Synthesis. By W. CARRUTHERS (University of Exeter). Cambridge University Press, London. 1971. x + 399 pp. $16.50 (hardcover); $5.95 (paperback).

This recent addition to the Cambridge Chemistry Texts Series provides a survey of the more important new methods in synthetic organic chemistry. The treatment is necessarily brief and the emphasis is on synthetic utility rather than reaction mechnisms. The book is organized into seven chapters with the following headings: Formation of Carbon–Carbon Single Bonds, Formation of Carbon–Carbon Double Bonds, The Diels–Alder Reaction, Reactions at Unactivated C–H Bonds, Synthetic Applications of Organoboranes, Oxidation, Reduction. The nearly 400 references that are included represent a good combination of pertinent review articles and very recent work. In the opinion of this reviewer, the author has been eminently successful in his aim to prepare a text for advanced undergraduates and beginning graduate students. These and other "students" of synthetic organic chemistry should find this book extremely useful.

Robert E. Gilman, *Rochester Institute of Technology*

Physics of Electronic Ceramics. Edited by L. L. HENCH and D. B. DOVE (University of Florida). Marcel Dekker, New York, N. Y. 1971–1972. Part A: xviii + 564 pp. $29.50. Part B: xx + 552 pp. $29.50.

The two parts of this volume cover the proceedings of the Electronics Phenomena in Ceramics Conference held at the University of Florida in 1969. The purpose of the conference and of these volumes is to provide a review of the electronic and structural properties of metal oxides and related material as well as to present some commercial applications of these materials. In this respect the editors and the conference organizers have done an admirable job. A perusal of both parts shows that the editors have gone to a considerable effort of bringing together experts in every conceivable aspect of ceramic theory and methodology.

Part A is divided into six parts: a brief introduction to the overall picture of quantum mechanical applications to ceramics; electronic and defect properties of *crystalline* ceramics; electronic processes in *amorphous* ceramics; thin-film structure and technology, surface structure, and dielectric properties. Part B continues with four more sections on static and dynamic properties of ferroelectrics, magnetic structure of ceramics, optical properties of ceramics, and related phenomena and concludes with device applications of crystalline and amorphous ceramics.

These volumes will thus serve as an extremely useful introduction to those physicists, chemists, and materials science engineers who wish to become acquainted with the theory and technology of metal oxides.