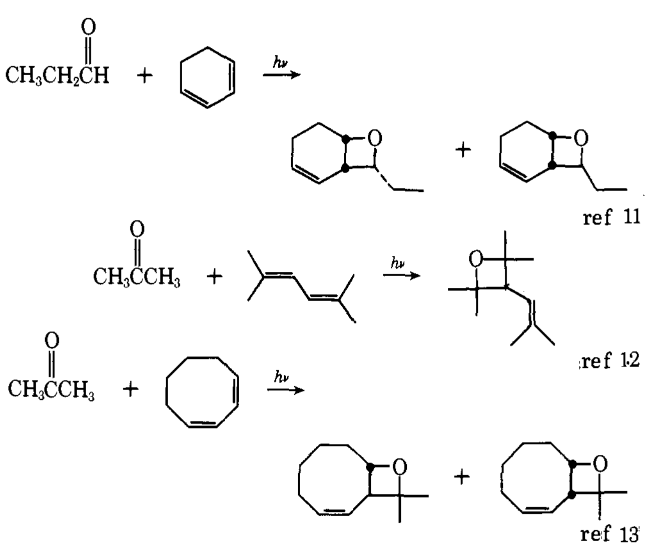

and 2,5-dimethyl-2,4-hexadiene. A mechanism consistent with all of these observations involves the formation of a charge-transfer stabilized exciplex which can collapse to vinyl oxetanes or undergo radiationless decay to the ground-state molecules, a process which is seemingly favorable for exciplexes. Examination of data from the literature on the variation of quantum yield for oxetane formation as a function of diene concentration, in combination with our values for the singlet lifetimes, yields rate constants for exciplex formation assuming this mechanism. The value of $4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ so obtained from the data of Kubota and coworkers[11] is in good agreement with our value of $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for the propionaldehyde–cyclohexadiene system. A similar analysis using the data of Barltrop and Carless[12] for the acetone–dimethylhexadiene study gives rise to a rate constant of $7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ which is in poorer agreement with our value from fluorescence quenching of $1.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. It is possible that an experimental anomaly arising from consumption of the diene during the experiment (disproportionately affecting the results obtained at low diene concentrations) can account for this discrepancy.[14] The example involving acetone and cyclohexadiene, however, cannot be accommodated by a mechanism involving the singlet state of the ketone. The rate constant obtained from analysis of the data of Shima and coworkers[13] is $3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. Our fluorescence experiments show that the singlet state of acetone is quenched by 1,3-cyclohexadiene with a rate constant of only $7 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. Thus, we feel that oxetane formation in the latter case occurs predominantly from the triplet state of acetone. The fact that a chemical reaction can compete with triplet energy transfer to cyclooctadiene probably again reflects the decrease in diene character for the eight-membered ring.

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(14) We wish to thank Professor N. C. Yang for pointing out this possible explanation to us, for a preprint of his unpublished work on quenching of alkanone singlets by dienes, and for stimulating discussions concerning the mechanism of the quenching action; N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971).

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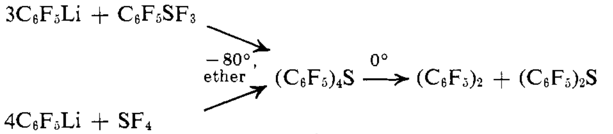
Tetraarylsulfuranes

Sir:

Tetrakis(pentafluorophenyl)sulfurane (**1**), the first observed pentacoordinated sulfur derivative with four carbon–sulfur bonds, has been prepared in solution at −80° from the reaction of (pentafluorophenyl)lithium with (pentafluorophenyl)trifluorosulfurane or sulfur tetrafluoride. At 0° it decomposes to decafluorobiphenyl and bis(pentafluorophenyl) sulfide.



$$\left.\begin{array}{l}3C_6F_5Li + C_6F_5SF_3 \\ \\ 4C_6F_5Li + SF_4\end{array}\right\} \xrightarrow[\text{ether}]{-80^\circ,} (C_6F_5)_4S \xrightarrow{0^\circ} (C_6F_5)_2 + (C_6F_5)_2S$$

1

Recently, considerable interest has developed in pentacoordinated sulfur compounds (sulfuranes),[1,2] particularly as intermediates in the reaction of organolithiums with arylsulfonium salts.[1] However, only sulfuranes with a minimum of two electronegative noncarbon ligands, such as phenyltrifluorosulfurane[3] or dialkoxydiarylsulfurane,[2b] have been isolated. Earlier we found that phenyltrifluorosulfurane or sulfur tetrafluoride reacted vigorously with phenyllithium to give diphenyl sulfide and biphenyl.[3] The recent studies by Trost[1] strongly support the postulate that tetraphenylsulfurane was formed, but direct detection is needed to show that the sulfurane exists as an intermediate and not just as a transition state. The marked effect of strong electron-withdrawing ligands in stabilizing four and six valence states of sulfur[4] suggested that the pentafluorophenyl group should be more effective than phenyl in stabilizing the sulfurane[5] and in addition provide a unique probe through ^{19}F nmr to detect intermediates stable only in solution at low temperature.

(Pentafluorophenyl)lithium reacts rapidly and exothermically with SF_4 or $C_6F_5SF_3$[6] at −80°. The solution gradually turns pale yellow and a white solid slowly precipitates. At concentrations higher than 5% considerable solid precipitates but redissolves to a great extent on warming to about −40°. The ^{19}F nmr resonance corresponding to the S–F fluorines disappears and only a single new set of pentafluorophenyl resonances is observed at −159.1, −151.9, and −140.1 ppm[7] in the ratio of 2:1:2 corresponding to the expected pattern for ortho, para, and meta. The ortho and meta peaks show no fine structure but are normal band width for pentafluorophenyl fluorines; the para resonance is a triplet, $J = 20$ Hz.[8] No

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(1) (a) B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969); (b) R. W. LaRochelle and B. M. Trost, *ibid.*, in press.

(2) J. C. Martin and R. J. Arhart (a) *ibid.*, **93**, 2339 (1971); (b) *ibid.*, **93**, 2341 (1971); (c) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

(3) W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3058 (1962).

(4) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(5) The σ_I value for C_6F_5 is 0.25 *vs.* 0.08 for C_6H_5: W. A. Sheppard, *J. Amer. Chem. Soc.*, **92**, 5419 (1970).

(6) (Pentafluorophenyl)trifluorosulfurane ((pentafluorophenyl)sulfur trifluoride) was prepared by reaction of silver difluoride with bis(pentafluorophenyl) disulfide by the procedure reported for preparation of arylsulfur trifluorides.[3]

(7) Measured from 5% internal C_6F_6 and corrected to standard scale by subtracting 163.0 ppm.

(8) A first-order coupling for the para fluorine is often observed for the pentafluorophenyl system but the meta and ortho fluorines usually have complex patterns.

significant change in the spectra is observed until the solution is warmed to almost 0°, when the original set gradually disappears as new peaks appear at -161.8, -151.6 to -150.0, -138.3, and -132.6 to -132.2 ppm; the new spectra correspond exactly to that of a 1:1 mixture of decafluorobiphenyl and bis(pentafluorophenyl) sulfide. The main reaction solution was warmed and distilled, and the residue was analyzed by gc and ir. The yields were decafluorobiphenyl, 70%, bis(pentafluorophenyl) sulfide, 71%, and approximately 20% of by-products, chiefly two higher boiling components. The ^{19}F spectrum was unchanged on addition of excess styrene or norbornene at $-80°$. The decomposition in the presence of these olefins occurred at 0° to give similar yields of decafluorobiphenyl and bis(pentafluorophenyl) sulfide and no new products. Solutions from the reaction of (pentafluorophenyl)lithium with the sulfur fluorides also decomposed at $-80°$ in 1–3 days to give the same products. The sulfurane could be purified at $-80°$ by filtration and re-solution in tetrahydrofuran or trichlorotrifluoromethane but the purified material also decomposed at -20 to 0° like that in ether solution.

Further evidence for the presence of a new sulfur compound at $-80°$ was the uv absorption at 2580 Å ($\epsilon \sim 77{,}000$) compared to $(C_6F_5)_2$, 2650 (1800) and 2300 Å (13,000), and $(C_6F_5)_2S$, 2650 (6200), 2430 (8700), and 2310 Å (10,500). Also, the ir on the ether solution at $-80°$ showed absorption at 10.46, 13.50, and 13.92 μ that did not appear in an ether solution of decafluorodiphenyl and/or bis(pentafluorophenyl) sulfide.

The spectral data and the characterization of the decomposition products strongly support the formation of the new sulfurane **1**. This sulfurane is proposed to have a rapidly pseudorotating[9] trigonal-bipyramid structure (because of the single set of pentafluorophenyl peaks with no indication of broadening) and to decompose by an intramolecular process. The stabilization of this sulfurane could be the result of (1) lowering the ground-state energy through the electron-withdrawing effect of the four pentafluorophenyl substituents, or (2) raising the barrier to collapse to biphenyl and sulfide, or (3) a combination of both. Factor 1 may result from increased participation of d orbitals in bonding because d orbitals are contracted by the electronegative ligands,[4] or by more effective conjugation of an unshared electron pair with the pentafluorophenyl ring (note upfield shift of ortho and para fluorines relative to bis(pentafluorophenyl) sulfide). An increased barrier to collapse could result from steric or electronic repulsion of the ortho fluorines damping the vibration that leads to carbon–carbon bond formation. The fluoride ion by-product could be involved in the apparent rapid "pseudorotation," possibly by complexing to form an R_4SF^- intermediate that would have elements of symmetry such that the pentafluorophenyl groups would be equivalent.[10]

This new pentacoordinated sulfurane should provide the opportunity to answer the many mysteries of sulfuranes. In collaboration with Professor B. M. Trost, we plan to determine structure, mechanism of decomposition, and stability *vs.* substituents and complexing agents, in order to answer the questions of when and where sulfuranes are intermediates and how they compare with the more stable pentacoordinated phosphorus and selenium analogs.

Acknowledgment. We particularly thank Mrs. Jean Read, Mr. L. S. Walther, Miss Ellen Wallace, and Miss Carol Hermann for assistance in obtaining the spectral data at low temperature and Mr. Ed Wonchoba for assistance with the difficult synthetic manipulation.

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[9] K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970). A more general description is stereochemical nonrigidity indicating the molecule is undergoing rapid intramolecular rearrangement: E. L. Muetterties, *ibid.*, **3**, 266 (1970).

[10] Such an interaction could explain the catalysis of exchange in SF_4 and $C_6H_5SF_3$ by fluoride or hydrogen fluoride [ref 3 and see also E. L. Muetterties and R. A. Schunn, *Quart. Rev. Chem. Soc.*, **20**, 245 (1966)]. An SF_5^- was reported by reaction of CsF with SF_4 and was suggested to have the square pyramidal structure analogous to IF_5 with four equivalent fluorines (C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 357 (1964)).

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Book Reviews

Naturally Occurring Quinones. By R. H. Thomson (Aberdeen University, U. K.). Academic Press Inc., New York, N. Y. 1971. vii + 734 pp. £12.

This is the second edition of the book which was first published in 1957 by Butterworth. It is a larger work because it describes about 450 naturally occurring quinones, three times the number covered in the first edition. It is authoritative and it is well updated and revised with coverage of some new structural types of quinones.

Chapter 1 has been expanded to deal more adequately with biogenesis, and the wholly new Chapter 2 is devoted to modern methods of structure elucidation as applied to the quinones. Another new chapter deals with the anthracyclinones (naphthacenequinones of bacteria). The remainder of the book considers the individual quinones in groups as benzoquinones, naphthaquinones, anthraquinones, extended quinones, or miscellaneous quinones, as in the 1957 edition but in a more lucid style.

The work is well indexed and carries an Appendix to cover the literature up to early October 1970. It is recommended as an excellent introduction to a major group of natural pigments and should find itself in all chemical libraries.

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