Table I. Deuterium Isotope Effects in Singlet Oxygen Reactions by Intramolecular Competition (20–35°)[a]

Substrate	Generation of singlet O_2	Solvent	k_H/k_D
8	Seven sensitizers[b]	CH_3OH	1.80–1.96[c]
8	Methylene Blue	Pyridine	1.85
8	Two sensitizers[d]	Benzene	1.78–1.81
8	NaOCl, H_2O_2	$CH_3OH–H_2O$	2.37–2.42
9	Two sensitizers[e]	CH_3OH	1.28–1.43[c]
9	NaOCl, H_2O_2	$CH_3OH–H_2O$	1.76–1.77
10	Rose Bengal	CH_3OH	1.18–1.20[c]

[a] 2,4,6-Tri-*tert*-butylphenol was added as a radical inhibitor in most cases. [b] Methylene Blue, hematoporphyrin, Rose Bengal, Erythrosine B, Eosine Y, fluorescein, and riboflavin. [c] Assay by nmr gave k_H/k_D values that were *ca.* 0.1 lower for **9** and **10** and 0.4 lower for **8**. Similar values have been obtained by K. R. Kopecky, J. H. Van de Sande, and C. Mumford (*Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **16**, No. 4, A65 (1971)) in their nmr studies of isotope effects. [d] Zinc tetraphenylporphin and 1,8-dinaphthalenethiophene. [e] Methylene Blue and Rose Bengal.

Table I summarizes the results and reveals consistently low, positive k_H/k_D values under a variety of experimental conditions.[12] Low primary isotope effects (*cf.* Table I) for linear H transfer reactions are expected when the hydrogen in the activated complex is much more tightly bound to one atom than to the other.[13,14] This condition is met in the oxygenation transition state if the C–H bond is either weakened very little or is nearly broken,[15] and only the former possibility is compatible with our C–O stereochemical findings.

The combined stereochemical and isotope effect results therefore reveal a product-forming transition state in which oxygen, while bonded partially to olefinic carbon and to allylic C–H, has neither much perturbed the olefin geometry nor extensively weakened the C–H bond. Among other things, these findings clarify why thermodynamic stability of the final double bond has little effect on the reaction,[16] why conformational ring inversion (which sometimes must accompany a double bond shift) does not block oxygenation,[6b,c] and why the susceptibility of C–H to abstraction is not inherently related to whether it is primary, secondary, or tertiary.[2,17]

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[12] The slightly greater electron donor effect and slightly smaller size of CD_3 relative to CH_3 could influence the site of attack in the unsymmetrical olefin **8**, but not in **9**. We are currently studying intermolecular isotope effects to probe these points. Note that for a transition state that resembles reactant (*i.e.*, no hybridization change at CD_3) there should be virtually no secondary (*i.e.*, α) isotope effect (A. Streitwieser Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 80, 2326 (1958)).

[13] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); J. Bigeleisen, *Pure Appl. Chem.*, **8**, 217 (1964); R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).

[14] W. A. Pryor and K. G. Kneipp, *J. Amer. Chem. Soc.*, **93**, 5584 (1971).

[15] Bending modes could also be responsible for low isotope effects if the hydrogen has to be transferred *via* a severely angled transition state. However, More O'Ferrall has pointed out that six-membered cyclic transition states are not subject to such constraints, and Kwart and Latimore have presented experimental support for cases of cyclic transfer from oxygen to carbon. R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970); H. Kwart and M. C. Latimore, *J. Amer. Chem. Soc.*, **93**, 3770 (1971).

[16] *E.g.*, caryophyllene is only slightly more reactive than its less strained isomer isocaryophyllene (F. A. Litt and A. Nickon, *Advan. Chem. Ser.*, No. 77, 118 (1968)); terminal open-chain olefins and methylene cycloolefins react sluggishly. See ref 2a, b, g and K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965). See also behavior of germacrene (T. W. Sam and J. K. Sutherland, *J. Chem. Soc., Chem. Comm.*, 424 (1972)).

[17] Contrast the situation for homolytic cleavage of allylic C–H bonds. W. J. Farrissey, Jr., *J. Org. Chem.*, **29**, 391 (1964), and references cited therein.

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Some Reactions of Ground-State Magnesium Atoms

Sir:

There is no prior literature concerned with the reactions of ground-state atomic magnesium.

High vacuum (~10^{-5} Torr) evaporation of magnesium can be carried out essentially as was done with carbon,[1] from a resistively heated crucible to produce ground-state magnesium (^1S) or by arcing to produce in addition a population rich in metastable[2] excited state (^3P). We report here some reactions which occur on codeposition at liquid nitrogen temperature of ground-state magnesium atoms and a large excess of substrate (>100:1).

The codeposition of magnesium atoms with water at −196° results in greater than 90% yields of H_2 during the codeposition, 1 mol of H_2 per mol of Mg. The same hydrogen yields are obtained in codeposition of magnesium with anhydrous hydrogen bromide.

By contrast, codeposition with ammonia produces H_2 in only 2.4% yield and a bright maroon matrix. On slight warming the maroon is replaced by a briefly transient blue color before becoming colorless. During the warm-up, with pumping, 7–25% of the theoretical H_2 is released. The residue is mainly magnesium, since addition of deuterium oxide releases the hydrogen as greater than 80% D_2, and no NH_3, indicating only minor amounts of Mg–H, Mg–NH_3, or Mg–NH_2 are present. It will be reported elsewhere that excited state magnesium atoms show a different behavior.

Codeposition of magnesium atoms and neopentane produces a colorless matrix which deposits a film of metal on warming.

Alkyl halides codeposited with magnesium atoms produce a black matrix. Warm-up of the black matrices obtained from alkyl and aryl chlorides or bromides results in formation of colorless organomagnesium compounds, unsolvated Grignard reagents. Yields were determined by hydrolysis: *n*-propyl iodide, 76%; isopropyl bromide, 55%; *tert*-butyl bromide, 5%; chlorobenzene, 58%; vinyl bromide, 78% (latter product stable at −78°).

These organomagnesium compounds are not produced at −196°, but instead on warm-up. If the black matrix of *n*-propyl bromide and magnesium is prepared, the evaporation discontinued, and then methyl bromide is deposited on the black matrix, on warm-up methylmagnesium compounds are produced rather than propyl-. Further, if the propylmagnesium compound is

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[1] P. S. Skell, L. D. Wescott, J.-P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 2829 (1965).

[2] C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Washington, D. C., 1949, p 106.

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.

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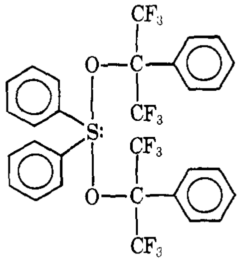
Sulfuranes. VIII. The Isolation and Characterization of a Dialkoxydiarylsulfurane Oxide, a Crystalline, Pentacoordinate Sulfur(VI) Species

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



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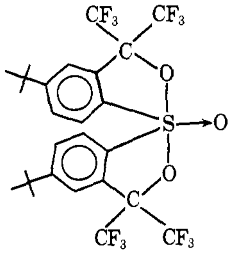

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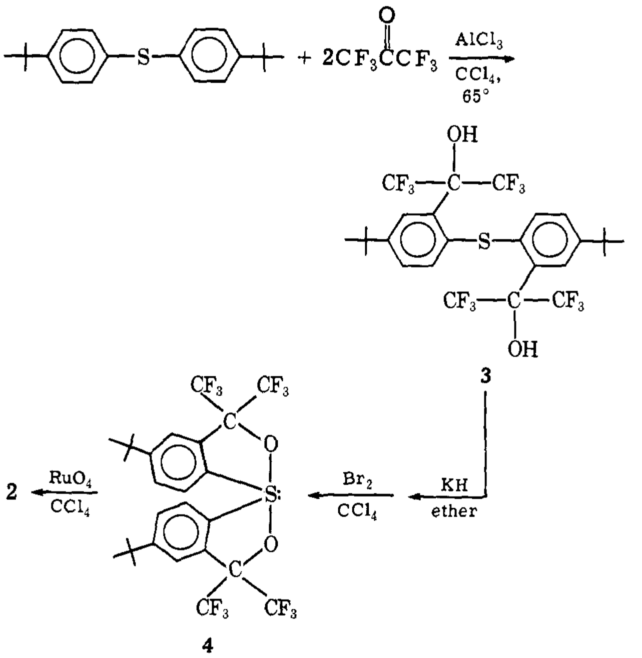
compound can be viewed as the ketal analog of a sulfoxide. We now report the first example of a ketal analog of a sulfone, compound **2**, which we shall call a dialkoxydiarylsulfurane oxide.

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 ($J_{\mathrm{FF}} = 9$ 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$_3$SO$_2$), and *m/e* 559 (15.94%, M − CF$_3$O). 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, $J_{\mathrm{AB}} = 9.3$ 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).