crude formulation of the metal-to-metal molecular orbitals arises from the overlap of the t_{2g} orbitals on the adjacent metal atoms. From a consideration of the appropriate overlap integrals, the order of molecular orbitals with increasing energy is $a_1' < e' < e'' < a_2''$, where the a_1' and a_2'' orbitals result from the symmetric and antisymmetric combinations of the trigonally directed d_{z^2} orbitals, and the e' and e'' orbitals are derived from similar combinations of the $t_{\pm}$ orbitals.[5,6] In the case of the $W_2Cl_9^{3-}$ anion, the electronic configuration is then $(a_1')^2(e')^4$. From the limited evidence available in the literature, it would appear that the $(a_1')^2(e')^2$configuration obtained from a two-electron oxidation is relatively unstable, and subsequent reactions lead to mononuclear W(IV) species.[7] Thus, the reaction of the anion with CN^- leads[8] to $W(CN)_8^{4-}$, while the pyrolysis in the presence of 8-hydroxyquinoline yields[9] the eight-coordinate, tetrakis derivative of W(IV).

We have now initiated an investigation of the $(a_1')^2(e')^3$ configuration. One-electron oxidation of the anion in dichloromethane occurs according to the equation

$$2W_2Cl_9^{3-} + X_2 \rightarrow 2W_2Cl_9^{2-} + 2X^-$$

$$X = Cl, Br, \text{and } I$$

and without the incorporation of the oxidant into the anion. The compound has been isolated as the violet $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$ with an effective magnetic moment of 1.87 BM per formula unit. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$: C, 32.80; H, 6.19; N, 2.39; Cl, 27.23; W, 31.38. Found: C, 33.11; H, 6.25; N, 2.38; Cl, 26.90; W, 30.86. The molar conductance of a solution of this compound in acetonitrile (4.41×10^{-4} *M*) at 25° is 315 ohm^{-1} cm^2 $mole^{-1}$, which compares favorably with the molar conductivities of $Re_2Cl_9^{2-}$, $Re_2Br_9^{2-}$, and $Re_2Cl_8^{2-}$ with the same cation.[10] The oxidation was easily followed spectrophotometrically by the disappearance of the intense band at 4640 Å which was complete upon the addition of 1 equiv of the halogen. The stoichiometry of the reaction was rigorously proven from the equation

$$\frac{A}{C_w} = \varepsilon_{3,3} - n\Delta\varepsilon\left(\frac{C_x}{C_w}\right)$$

where A is the absorbance at 4640 Å, C_w is the initial concentration of $W_2Cl_9^{3-}$, C_x is the number of moles of added halogen divided by the total volume, $\varepsilon_{3,3}$ and $\varepsilon_{3,4}$ are the molar extinction coefficients of $W_2Cl_9^{3-}$ and $W_2Cl_9^{2-}$, respectively, and $\Delta\varepsilon = \varepsilon_{3,3} - \varepsilon_{3,4}$. Using I_2 as the oxidant, a plot of the variables gave an intercept of 4370 for $\varepsilon_{3,3}$ (4390 observed) and a slope of 8080. From the assumed stoichiometry, $n = 2$ and therefore $\Delta\varepsilon = 4040$ (4070 observed). The final spectrum consisted of bands at 13,530 cm^{-1} (ε 1040) and 17,200 cm^{-1} (ε 1700) with a shoulder at 25,600 cm^{-1} ($\varepsilon \sim 618$). Further addition of halogen simply caused the intensity of the spectrum of the $W_2Cl_9^{2-}$ anion to decrease, until finally a colorless solution was obtained.

While the dinuclear nature of the anion is clear, the actual structure remains in some doubt. The far-infrared spectrum of $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$ has a band at 295 cm^{-1} and a shoulder at 306 cm^{-1}, while that of $[(n\text{-}C_4H_9)_4N]_3W_2Cl_9$ has a shoulder at 270 cm^{-1} and resolved bands at 280 and 300 cm^{-1}. It is possible that the bioctahedron structure has been retained, but other structures are also possible. For example, the oxidized species may have a structure derived from that of $Re_2Cl_8^{2-}$ by the attachment of a Cl atom along one end of the fourfold axis. A similar structure was included as a possibility for the $Re_2Cl_9^-$ anion.[10] However, $W_2Cl_9^{2-}$ is not isoelectronic with any known rhenium dinuclear species, so that corresponding structures are not necessarily expected.

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[4] R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

[5] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 68.

[6] Identical molecular orbitals have been proposed to account for the short Fe–Fe distance and the diamagnetism in $Fe_2(CO)_9$: L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," 2nd ed, Methuen and Co., Ltd., London, England, 1966, p 146.

[7] Pairwise interactions can exist in derivatives of W(IV), *viz.*, the tetrahalides. However, the reactions of the tetrahalides with a variety of ligands seem to invariably lead to mononuclear species.

[8] R. C. Young, *J. Am. Chem. Soc.*, **54**, 4517 (1932).

[9] R. D. Archer and W. D. Bonds, *ibid.*, **89**, 2236 (1967).

[10] F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).

Pentacoordinate Sulfur Compounds as Intermediates in Organic Reactions

Sir:

Much work has been performed on the mechanism of displacement reactions at sulfur.[1] One major question that remains unanswered is whether the pentacoordinate sulfur species represents an intermediate or a transition state. Earlier work[2-4] suggested the possibility of these types of intermediates in reactions of organolithium compounds with electron-deficient sulfur compounds, although this mode of reaction has been questioned.[4] We wish to report evidence strongly implicating pentacoordinate sulfur species as reaction intermediates as well as to establish a new synthetic method to effect coupling of two unsaturated fragments and to generate sulfur ylides, a versatile class of synthetic intermediates.

The reaction of triphenylsulfonium fluoroborate (I) with vinyllithium (II) generates diphenyl sulfide and styrene in quantitative yields (see Scheme I). Of the various reaction pathways, the most likely are (1) elimina-

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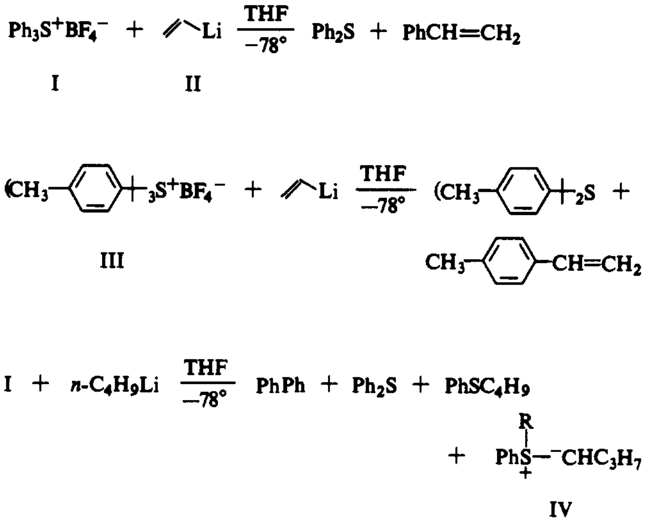
[1] (a) N. Kharasch, B. S. Thyagarajan, and A. I. Khodair, *Mechanisms Reactions of Sulfur Compd.*, **1**, 3 (1966); (b) C. R. Johnson and W. A. Phillips, *J. Org. Chem.*, **32**, 1926 (1967), and references therein.

[2] (a) B. M. Trost and R. C. Atkins, *Tetrahedron Letters*, 1225 (1968); (b) B. M. Trost and R. W. LaRochelle, *ibid.*, 3327 (1968).

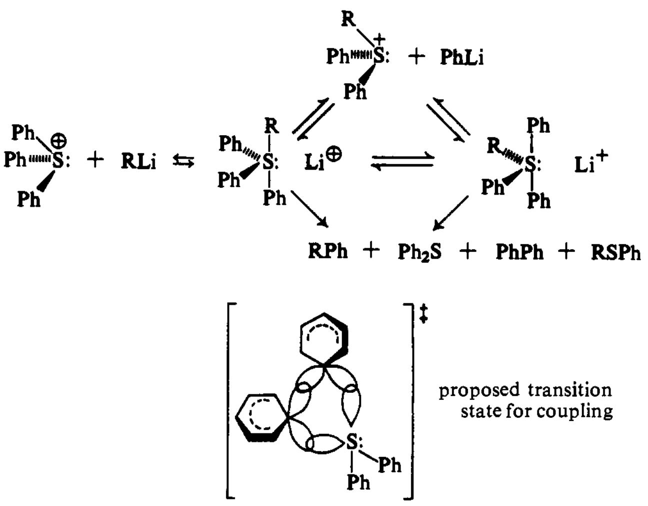
[3] (a) G. Wittig and H. Fritz, *Ann.*, **577**, 39 (1952); (b) V. Franzen, H. I. Joschek, and C. Mertz, *ibid.*, **654**, 82 (1962). For other reactions that may involve pentacoordinate sulfur species see (a) K. K. Andersen and N. E. Papanikolaow, *Tetrahedron Letters*, 5445 (1966); E. N. Givens and H. Kwart, *J. Am. Chem. Soc.*, **90**, 378 (1968); W. A. Sheppard, *ibid.*, **84**, 3058 (1962); E. Winterfeldt, *Chem. Ber.*, **98**, 1581 (1965).

[4] (a) V. Franzen and C. Mertz, *Ann.*, **643**, 24 (1961); (b) K. K. Andersen and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).

Scheme I. Reaction of Organolithium with Sulfonium Salts



Scheme II. Mechanistic Interpretation

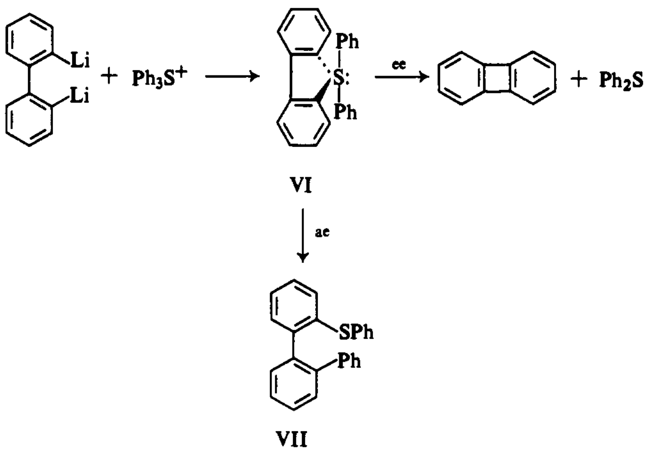


tion to benzyne followed by addition of the organolithium, (2) addition to the aromatic ring followed by elimination, (3) addition to sulfur followed by concerted fragmentation, and (4) electron transfer to sulfur from the organolithium followed by radical extrusion and subsequent radical–radical coupling. The benzyne mechanism seems highly unlikely since it requires 2 equiv of organolithium/equiv of I whereas reaction of equimolar amounts of I and II produced quantitative yields of products. Further evidence eliminating the benzyne route derives from the reaction of II with tri-*p*-tolysulfonium fluoroborate. If the aryne were involved as an intermediate in the reaction, *m*-methylstyrene would be the predominant product.[5] None of this isomer was produced. Similarly, reaction of III with phenyllithium produced only biphenyl, *p*,*p*′-dimethylbiphenyl, and *p*-methylbiphenyl as the hydrocarbon products. No *meta* isomers were detected.

The addition–elimination and the electron-transfer mechanisms were ruled out by careful examination of the reaction of *n*-butyllithium with I. The only hydrocarbon coupling product was biphenyl in 30–40% yield.[6a] If the addition–elimination mechanism were operative, the more nucleophilic *n*-butyllithium should produce at least as much of its coupling product, *n*-butylbenzene, as in the vinyllithium case. Furthermore, if electron-transfer reactions were involved, the fact that *n*-butyllithium should be a better electron donor than vinyllithium again would lead to the expectation of at least as much coupling leading to *n*-butylbenzene as in the vinyllithium case. The lack of *n*-butylbenzene argues strongly against these mechanisms. One of the products of this reaction is the sulfonium butylide IV (R = Ph and *n*-C_4H_9). Quenching the mixture with cyclohexanone before work-up led to 1-oxa-2-*n*-propylspiro[2.5]octane in approximately 40% yield. Since triphenylsulfonium bromide is commercially available, this *in situ* method to form substituted ylides is an attractive alternative to preformation of the alkylsulfonium salt, particularly in those cases where such salts are very unstable and difficult to handle.[6]

A reasonable mechanism that accounts for all the above data is the formation of the pentacoordinate sulfur species V (see Scheme II).[7] The reversibility of the addition is suggested by the fact that ligand exchange accompanies the coupling reaction.[8] Coupling involves overlap of the π systems of two of the ligands with concomitant cleavage of the carbon–sulfur bonds. The preferred vinyl-phenyl coupling over phenyl-phenyl coupling arises since the latter requires destruction of the aromaticity of two benzene rings in the transition state, whereas the former requires only one.

Scheme III. Stereochemistry of Coupling



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[5] (a) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1968); (b) G. B. R. de Graaff, H. J. den Hertog, and W. C. Melger, *Tetrahedron Letters*, 963 (1965).

[6] (a) Our results do not agree with a report by Franzen, *et al.* Although the reaction appears in the discussion in this paper, there is no corresponding description in the Experimental Section: V. Franzen, H. I. Joschek, and C. Mertz, *Ann.*, **654**, 82 (1962); (b) *cf.* V. Franzen, H. J. Schmidt, and C. Merz, *Chem. Ber.*, **94**, 2942 (1961).

[7] The trigonal-bipyramid structure for the pentacoordinate sulfur species is assumed based on the known structures of sulfur tetrafluoride and alkylsulfur trifluorides. See (a) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964). (b) For a recent discussion of the geometry of pentacoordinate group V and VI elements see A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6675 (1968).

[8] The available evidence does not demand that ligand exchange proceed through the pentacoordinate sulfur species, but the occurrence of this species as an intermediate in the coupling reaction suggests a similar pathway for the ligand exchange. From the available data, it is apparent that the activation energy for ligand exchange and coupling must be comparable. In the vinyllithium with triphenylsulfonium salt case, no exchange occurs, only coupling, whereas, in the *n*-butyllithium case, ligand exchange is faster than coupling by about a factor of 2. This change in relative activation energies is quite understandable in light of the fact that in the latter case, where phenyl–phenyl coupling is involved, the aromaticity of two rings must be destroyed.

A stereochemical requirement for the coupling reaction was suggested by the examination of the reaction of 2,2′-dilithiobiphenyl with triphenylsulfonium salt. The reaction involves initial ligand exchange to produce 2-(2′lithiobiphenyl)diphenylsulfonium salt followed by ring closure to VI. For steric and electronic reasons, the biphenylyl group would prefer the diequatorial position. If equatorial–equatorial (ee) coupling occurred, the products would be biphenylene and diphenyl sulfide, whereas apical–equatorial (ae) coupling leads to VII. The formation of VII as the exclusive product derived from VI is indicative of preference for ae coupling.

These reactions are strikingly similar to the reactions of pentavalent phosphorus, lending further support to the above interpretations.[9]

Acknowledgment. We wish to express our thanks to the National Institutes of Health for support of this work.

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(9) D. Seyferth, T. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, **88**, 2207 (1966), and references therein.

(10) Alfred P. Sloan Foundation Fellow.

(11) National Institutes of Health Predoctoral Fellow.

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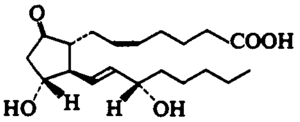
The Structure of the Major Urinary Metabolite of Prostaglandin E_2 in Man

Sir:

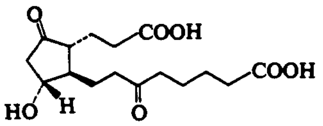
A urinary metabolite of prostaglandin E_2[1] (**1**) in the guinea pig was recently identified as 5β,7α-dihydroxy-11-ketotetranorprostanoic acid.[2] We now report the structure of the major urinary metabolite (**2**) formed from prostaglandin E_2 (**1**) in man.

[17,18-$^3H_2$]Prostaglandin E_2[3] (5.8 μg, specific activity 420 μCi/μmol) was injected intravenously into male subjects. Of the injected radioactivity, about 50% could be recovered in the urine during the first 5 hr and less than 3% during the following 12 hr. The first portion of radioactive urine was added to about 10 l. of urine, and 1-l. samples of this pool were processed as described below.

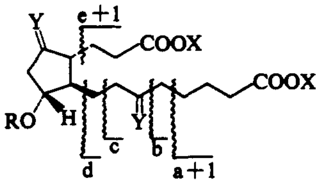
After acidification of the urine, 75–85% of the radioactivity could be extracted with three portions of ethyl acetate. This extract was subjected to reversed-phase partition chromatography.[4] The material in the main peak of radioactivity (200–300 ml of effluent) was treated with diazomethane or diazoethane and was again subjected to reversed-phase partition chromatography.[4] The dimethyl ester **3** (114–156 ml of effluent) and the diethyl ester **4** (168–216 ml of effluent) were then purified by silicic acid chromatography (eluted with ethyl acetate–benzene, 60:40). The esters were subsequently converted into O-methyloxime derivatives and subjected to trimethylsilylation or acetylation. The methods used to prepare the derivatives **5**–**8** have been described previously.[5,6] Reduction of **3** with sodium borohydride in methanol yielded **9**, from which the triacetate **10** was prepared by treatment with acetic anhydride–pyridine. Reduction of **3** with sodium borodeuteride yielded **11**, which was acetylated to afford **12**.



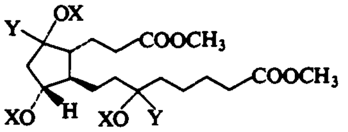
1



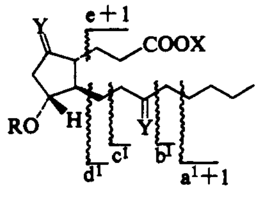
2



3, X = CH_3; Y = O; R = H
4, X = C_2H_5; Y = O; R = H
5, X = CH_3; Y = CH_3ON; R = CH_3CO
6, X = CH_3; Y = CH_3ON; R = $Si(CH_3)_3$
7, X = CH_3; Y = C^2H_3ON; R = $Si(CH_3)_3$
8, X = C_2H_5; Y = CH_3ON; R = $Si(CH_3)_3$



9, X = H; Y = H
10, X = CH_3CO; Y = H
11, X = H; Y = ^2H
12, X = CH_3CO; Y = ^2H



13, X = H; Y = O; R = H
14, X = CH_3; Y = CH_3ON; R = CH_3CO
15, X = CH_3; Y = CH_3ON; R = $Si(CH_3)_3$
16, X = C_2H_5; Y = CH_3ON; R = $Si(CH_3)_3$

7α-Hydroxy-5,11-diketotetranorprostanoic acid (**13**) and the derivatives **14**, **15**, and **16** were prepared[5] for use as references in the analysis by gas–liquid partition chromatography–mass spectrometry.

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(1) Prostaglandin E_2 is the trivial name for 11α,15-dihydroxy-9-keto-prosta-5-*cis*,13-*trans*-dienoic acid.

(2) M. Hamberg and B. Samuelsson, *Biochem. Biophys. Res. Commun.*, **34**, 22 (1969).

(3) E. Änggård, K. Gréen, and B. Samuelsson, *J. Biol. Chem.*, **240**, 1932 (1965).

(4) Reversed-phase partition chromatography of ethyl acetate extracts of urine was carried out using columns of 45 g of hydrophobic Hyflo SuperCel and solvent system D supplemented with acetic acid (*cf.* A. Norman, *Acta Chem. Scand.*, **7**, 1413 (1953), and ref 5). Reversed-phase partition chromatography of **3** and **4** was performed with columns of 9 g of hydrophobic Hyflo SuperCel and solvent system F-58 supplemented with acetic acid (*cf.* ref 5).

(5) M. Hamberg, *European J. Biochem.*, **6**, 135 (1968).

(6) $C^2H_3ONH_2 \cdot HCl$ was synthesized by treating $HON(SO_3K)_2$ (F. Raschig, *Ber.*, **40**, 4580 (1907)) with C^2H_3I.