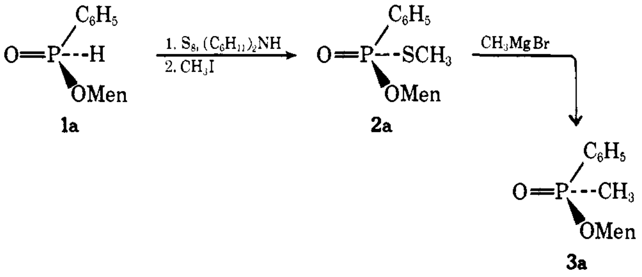
the resultant menthyl *S*-methyl phenylphosphonothioate (**2a**) with methylmagnesium bromide to give menthyl $(R)_P$-methylphenylphosphinate (**3a**), proceeds with *overall* retention of configuration.[7a] An X-ray analysis, described below,[7b] establishes the chirality at phosphorus in the intermediate phosphonothioate **2a** as *S*. It follows that the Grignard displacement reaction **2** → **3** and the thiomethylation **1** → **2** must both proceed with retention of configuration at phosphorus.[8,10]



1a **2a** **3a**

Crystals suitable for X-ray analysis were obtained by slow evaporation of a 2,2,4-trimethylpentane solution of **2a**, mp 76.5°, $[\alpha]D$ −141° (benzene).[7a] Precession photographs on a crystal of dimensions *ca.* 0.15 × 0.45 × 0.10 mm showed that the diastereomer crystallizes in the monoclinic system; the only extinction observed was $0k0$ with k odd. Least-squares refinement of the observed spacings of eight hkl reflections measured on a Picker automatic four-circle diffractometer gave lattice constants of $a = 18.076 \pm 0.013$, $b = 6.763 \pm 0.003$, $c = 8.509 \pm 0.010$ Å, $\beta = 102.30 \pm 0.01°$. The experimentally determined density of 1.15 g cm^{-3} agrees well with the value 1.10 g cm^{-3} calculated for two molecules of **2a** per unit cell. Since the molecule is chiral, the space group is determined uniquely as $P2_1$-C_2^2. A total of 1519 reflections above background up to $2\theta = 120°$ was observed with Cu Kα radiation using the θ-2θ scan mode on the above diffractometer. Monitoring of three standards during the data collecting showed no significant decay. The structure was solved by Patterson and Fourier methods. The final value of R in least-squares refinement which allowed for anisotropic thermal motion of the four heaviest atoms and for isotropic motion of the 17 carbon atoms, and which ignored the hydrogen atoms, is 10.3%. A view of the molecule along the b axis is shown in Figure 1. The configuration of (−)-menthol, used in the preparation of **2**, is 1*R*, 3*R*, 4*S*,[11] and it follows that the configuration at phosphorus is *S*.

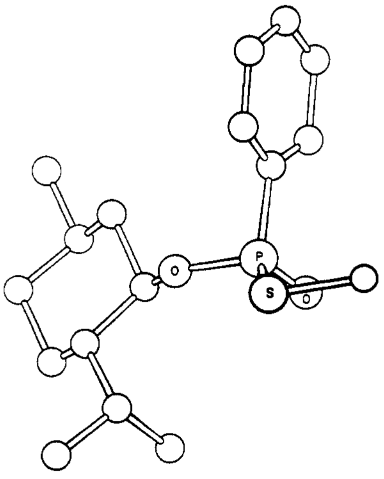


Figure 1. Menthyl *S*-methyl $(S)_P$-phenylphosphonothioate (**2a**) as viewed along the *b* axis of the crystal. Unlabeled atoms are carbon. The hydrogen atoms have been omitted.

It is reasonable to extend the present conclusions to the analogous *methyl*phosphinate systems.[12] Consequently, the absolute configuration of isopropyl *S*-methyl methylphosphonothioate (**5**)[3] is now in question, as are the underlying assumptions[2] which led to this assignment. It further follows that assignments of absolute configurations to sarin and other anticholinesterases,[3] to isopropyl methylphosphinate and its derivatives,[14] and to *O*-ethyl ethylphosphonothioic acid,[15] all of which depend upon the assignment of **5**, must now be reassessed.

Studies are underway to examine the effect of diverse nucleophilic reagents and leaving groups on the stereochemical course of displacement reactions at phosphorus in phosphonothioates and related systems.

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(7) (a) W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *Chem. Commun.*, 605 (1971). Overall retention was also observed for the sequence $(S)_P$-**1** (**1b**) → **2b** → $(S)_P$-**3** (**3b**). (b) A listing of observed and calculated structure factors for menthyl *S*-methyl phenylphosphonothioate will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $6.00 for photocopy or $2.00 for microfiche.

(8) A direct configurational link between structures determined by X-ray diffraction is provided by the reaction of diastereomerically pure **2a** with *n*-propylmagnesium bromide, which gives diastereomerically pure menthyl $(R)_P$-phenyl-*n*-propylphosphinate (**4a**); similar treatment of **2b** affords **4b**. The chirality at phosphorus in **4a** is *R*, as determined by X-ray analysis.[9]

(9) E. B. Fleischer and R. Dewar, unpublished results reported in footnote 10 of ref 5a.

(10) Treatment of diastereomerically pure **2a** with methyllithium in tetrahydrofuran gives diastereomerically pure **3a**. Retention stereochemistry of the displacement reaction is therefore not limited to Grignard reagents.

(11) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953); numbering of carbons as in *p*-menthan-3-ol. See also R. Parthasarathy, J. Ohrt, A. Horeau, J. P. Vigneron, and H. B. Kagan, *Tetrahedron*, **26**, 4705 (1970).

(12) It has been recognized,[7a,13] that transformation of menthyl methylphosphinate to **3** by way of the intermediate menthyl *S*-methyl methylphosphonothioate (*i.e.*, the *P*-methyl analog of **2**) also occurs with overall retention of configuration.

(13) G. R. Van den Berg, D. H. J. M. Platenburg, and H. P. Benschop, *Chem. Commun.*, 606 (1971).

(14) L. P. Reiff and H. S. Aaron, *J. Amer. Chem. Soc.*, **92**, 5275 (1970); L. J. Szafraniec, L. P. Reiff, and H. S. Aaron, *ibid.*, **92**, 6391 (1970); L. P. Reiff, L. J. Szafraniec, and H. S. Aaron, *Chem. Commun.*, 366 (1971).

(15) M. Mikolajczyk and M. Para, *ibid.*, 1192 (1969).

(16) Public Health Service Predoctoral Fellow, 1969–1971.

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Hydride Derivatives of Niobocene and Tantalocene

Sir:

The surprising C_6H_6-D_2 exchange catalyzed by $(C_5H_5)_2TaH_3$[1] has stimulated interest in synthesis of

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(1) E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970).

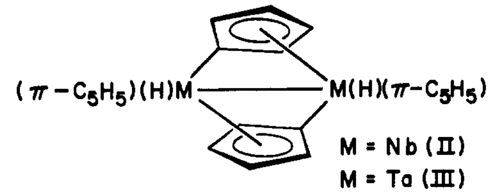


Figure 1. The bridging system proposed for $[(C_5H_5)(C_5H_4)NbH]_2$ and its tantalum analog.

the corresponding niobium hydride.[2] We have now prepared $(C_5H_5)_2NbH_3$ (I) and find that its chemistry is extraordinarily rich and varied.[3]

Compound I was prepared by heating a mixture of niobium pentachloride, cyclopentadienylsodium, and sodium borohydride under 800 atm hydrogen pressure in toluene. The solution was filtered and evaporated to give 20–30% crude $(C_5H_5)_2NbH_3$ which was recrystallized from toluene. The presence of Nb–H bonds is indicated by a metal–hydrogen stretching absorption in the infrared spectrum at 1710 cm^{-1} and by proton nmr resonances (toluene-d_8 solution) at τ 12.73 and 13.72 with an area ratio of 1:2 (in addition to a C_5H_5 resonance at τ 5.20 of area 10). The structure of $(C_5H_5)_2NbH_3$ is thus closely related to that of $(C_5H_5)_2TaH_3$.[4]

When I is heated in benzene at 80°, hydrogen is rapidly evolved and exchange between H_2 and benzene-d_6 occurs. Heating I with triethylphosphine produces $(C_5H_5)_2Nb(H)(PEt_3)$. In these respects the chemistry of I parallels that of $(C_5H_5)_2TaH_3$.[1] The outstanding difference in the two species is the great reactivity of the niobium trihydride. In reactions which proceed with loss of hydrogen from the trihydride, rates at 80° for the niobium complex exceed those for the tantalum analog by an order of magnitude.

Thermal decomposition of I in benzene at 80° yields a yellow solid with the composition corresponding to "niobocene," $(C_5H_5)_2Nb$. However, it is best formulated as a hydride-containing dimer $[(C_5H_5)(C_5H_4)NbH]_2$ (II).[5] Decomposition of $(C_5H_5)_2TaH_3$ produces the tantalum analog, $[(C_5H_5)(C_5H_4)TaH]_2$ (III), which is isomorphous with the niobium dimer and has similar spectral properties. Both dimers are diamagnetic. Based on the nmr spectra we propose that these new metallocene derivatives contain bridging C_5H_4 groups which interact with the metal atoms in both σ- and π-bonding capacities (Figure 1). The nmr spectrum of II contains a normal C_5H_5 resonance at τ 5.11. Of the C_5H_4 protons, one appears at low field (τ 3.95), while the remaining three are clustered about τ 5.6.[6] The spectrum of the bridging C_5H_4 group in $(C_5H_5)(CO)Mo–C_5H_4–Mn(CO)_4$[7] does not appear to be perturbed in this manner. Recently "titanocene" has been formulated as a hydride-bridged dimer, $[(C_5H_5)(C_5H_4)TiH]_2$.[8] Our finding supports the proposal that the titanium dimer contains bridging C_5H_4 groups[7] in addition to the hydride bridges.

Treatment of II in benzene solution with 800 atm of hydrogen at 80° converts it quantitatively to I. The equilibria present presumably are those in eq 1. Although IV was not isolated, it is a likely intermediate in the formation of II as well as in C_6H_6–D_2 exchange[1] and in formation of $(C_5H_5)_2NbH(L)$ (L = R_3P, CO, C_2H_4).

$$\underset{\text{I}}{(C_5H_5)_2NbH_3} \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} \underset{\text{IV}}{[(C_5H_5)_2NbH]} \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} \underset{\text{II}}{[(C_5H_5)(C_5H_4)NbH]_2} \quad (1)$$

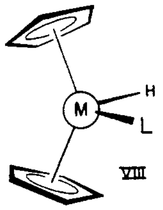
$$\text{IV} \xrightarrow{C_2H_4} \underset{\text{V}}{(C_5H_5)_2NbH(C_2H_4)} \quad (2)$$

$$\text{V} \rightleftharpoons \underset{\text{VI}}{[(C_5H_5)_2NbC_2H_5]} \underset{-C_2H_4}{\overset{C_2H_4}{\rightleftharpoons}} \underset{\text{VII}}{(C_5H_5)_2Nb(C_2H_4)(C_2H_5)} \quad (3)$$

$$\text{VI} + H_2 \rightleftharpoons [(C_5H_5)_2NbH_2C_2H_5] \longrightarrow C_2H_6 + \text{IV} \quad (4)$$

Ethylene and $(C_5H_5)_2NbH_3$ react in solution to form the ethyl–ethylene complex VII, presumably by reactions 2 and 3. When the reaction is carried out with a limited amount of C_2H_4, it is possible to crystallize a hydrido–ethylene complex (V), a species often postulated as an intermediate in catalytic reactions of ethylene but seldom isolated.[9] When hydrogen and excess ethylene are added to the system, ethylene is catalytically reduced to ethane. This reaction probably involves the ethyl derivative VI as a key intermediate (analogous to IV) in the catalytic cycle of eq 2–4. (The species in brackets were not isolated.) Comparable equilibria apparently exist for both the tantalum and niobium systems, since the tantalum analog of VII has been isolated and $(C_5H_5)_2TaH_3$ acts as an ethylene hydrogenation catalyst.

From spectral data (Table I) the new compounds $(C_5H_5)_2M(H)(L)$ are best represented by structure VIII,



VIII

analogous to the geometry of $(C_5H_5)_2MoH_2$.[10]

Reactions of the dienes allene and butadiene with I occur with reduction of olefin to the saturated hydrocarbon and formation of the π-allyl complex $(C_5H_5)_2Nb(\pi\text{-}C_3H_5)$ (IX)[11] and the π-crotyl complex $(C_5H_5)_2Nb(\pi\text{-}C_4H_7)$ (X), respectively. The nmr spectrum of X shows nonequivalent cyclopentadienyl groups and

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[2] "Niobocene," $(C_5H_5)_2Nb$, and $(C_5H_5)_2NbH_3$ have been disclosed without experimental support: U. S. Patent 2,921,948 (1960) and U. S. Patent 3,288,829 (1966), respectively.

[3] Empirical composition has been established for all the reported compounds by elemental analysis and/or mass spectra.

[4] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

[5] Spectral data are: ir 1680 cm^{-1} (Nb–H stretching frequency), nmr (benzene-d_6 solution) τ 12.07 (Nb*H*, intensity 1 relative to the C_5H_5 and C_5H_4 resonances). *Anal.* Calcd for $C_{10}H_{10}Nb$: C, 53.84; H, 4.52; Nb, 41.65; mol wt (for $C_{20}H_{20}Nb_2$), 446. Found: C, 53.66; H, 4.55; Nb, 41.66; mol wt (for $C_{20}H_{20}Nb_2$), 483.

[6] Two of the three C_5H_4 protons near τ 5.6 (5.62, intensity 1, 5.66, intensity 2) are unresolved at a field strength of 220 MHz. In the spectrum of the tantalum analog III, each of the C_5H_4 protons appears as a separate resonance [benzene-d_6 solution, τ 5.22 (intensity 5, C_5H_5), 3.90, 5.72, 5.78, and 5.95 (each of intensity 1, C_5H_4), 11.09 (intensity 1, Ta*H*)].

[7] R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 93, 536 (1971).

[8] H. H. Brintzinger and J. E. Bercaw, *ibid.*, 92, 6182 (1970), and references therein.

[9] The first example of an isolable hydridoethylene complex was *trans*-$[PtH(C_2H_4)(PEt_3)_2]^+$: A. J. Deeming, B. F. G. Johnson, and J. Lewis, *Chem. Commun.*, 598 (1970).

[10] M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).

[11] F. W. Siegert and H. J. DeLiefde Meijer, *J. Organometal. Chem.*, 23, 177 (1970), have reported $(C_5H_5)_2Nb(\pi\text{-}C_3H_5)$ prepared from reaction of allylmagnesium bromide with $(C_5H_5)_2NbCl_2$.

Table I. Spectra of $(C_5H_5)_2M(H)(L)$ Compounds

Compound	Infrared ν_{M-H}	Infrared ν_{CO}	Nmr τ_{M-H}	Nmr J_{P-H}, Hz
$(C_5H_5)_2Nb(H)(CO$	1695	1900	16.39	
$(C_5H_5)_2Ta(H)(CO)$	1750	1885	16.80	
$(C_5H_5)_2Nb(H)(PMe_3)$	1635		17.84	27
$(C_5H_5)_2Nb(H)(PEt_3)$	1650		17.69	29
$(C_5H_5)_2Ta(H)(PEt_3)$	1705		19.54	21
$(C_5H_5)_2Nb(H)(C_2H_4)$	1735		12.95	

a pattern typical of the π-crotyl group. The position of the methyl group in X is syn with respect to the hydrogen on the central atom of the allylic system. The structure of X is thus like that of IX[11,12] and of 1,2-dimethylallyldicyclopentadienyltitanium.[13]

The original expectation that $(C_5H_5)_2NbH_3$, like $(C_5H_5)_2TaH_3$, would catalyze H-D exchange between H_2 and C_6D_6 has been realized. However, the two catalysts produce grossly different relative exchange rates with substituted benzenes.[14] These results will be reported in detail soon.

Acknowledgment. We are indebted to L. J. Guggenberger for initial and continuing crystallographic studies of the niobium dimer.

(12) H. J. DeLiefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, **4**, 651 (1970).

(13) R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Recl. Trav. Chim. Pays-Bas*, **86**, 1263 (1967).

(14) U. Klabunde, manuscript in preparation.

(15) Contribution No. 1809.

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Received April 26, 1971

Chemistry of Singlet Oxygen. XIV. A Reactive Intermediate in Sulfide Photooxidation[1]

Sir:

Dialkyl sulfides undergo sensitized photooxidation to give sulfoxides in a smooth reaction with overall stoichiometry[2,3]

$$2R_2S + O_2 \xrightarrow[\text{sens}]{h\nu} 2R_2\overset{+}{S}\text{—}\overset{-}{O}$$

We have previously reported that the reaction involves singlet oxygen (since it is competitively inhibited by singlet oxygen acceptors and quenchers), and that the reaction proceeds efficiently in methanol but very inefficiently in benzene.[3] In benzene, kinetic analysis shows that over 95% of the reactions of singlet oxygen with diethyl sulfide result in quenching, and only a few per cent lead to sulfoxide.[3] No quenching occurs in methanol. An attractive formulation for the reaction involves the intermediacy of an oxidizing species, which might be the zwitterion ("persulfoxide") **1**,[3,4] the diradical **2**,[2] or, possibly the cyclic peroxide **3**.

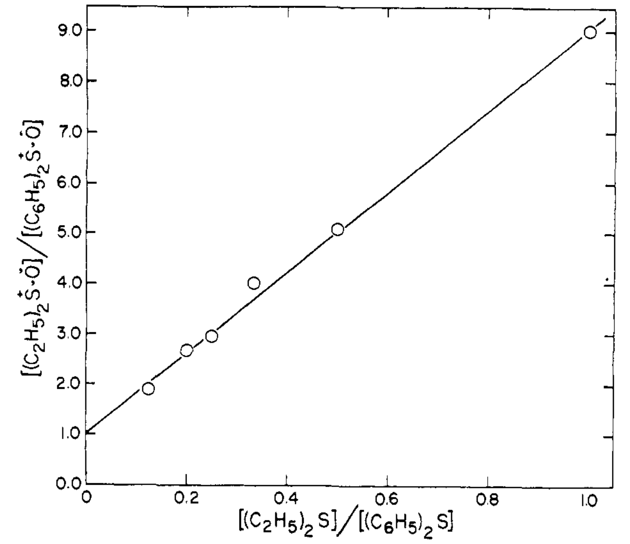
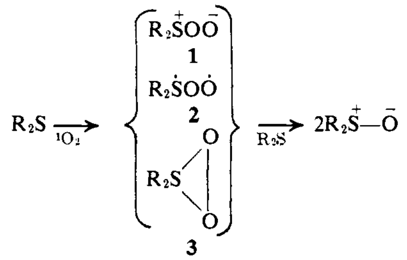
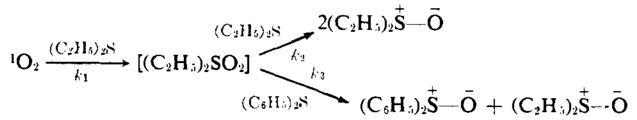


Figure 1. Photooxidation (methanol, rose bengal, 25°) of mixtures of diphenyl and diethyl sulfides: slope = 7.98 ± 0.38; intercept = 1.09 ± 0.17.

We wish to report experimental verification of an unstable reactive intermediate and tentatively assign it the persulfoxide structure **1**. The evidence for the intermediate is of three types.



1. **Trapping.** Diphenyl sulfide is virtually inert to photooxidation, producing diphenyl sulfoxide at a rate 2800 times slower than diethyl sulfide reacts to form diethyl sulfoxide under similar conditions (in methanol).[5] However, when mixtures of diphenyl and diethyl sulfides are irradiated, considerable amounts of diphenyl sulfoxide are formed. For instance, a solution of 0.02 *M* $(C_2H_5)_2S$ and 0.1 *M* $(C_6H_5)_2S$ in methanol (8 × 10^{-5} *M* in rose bengal) was irradiated for 1.25 min to produce a solution containing 3.64 × 10^{-3} *M* $(C_2H_5)_2S^+\text{-}O^-$ and 1.40 × 10^{-3} *M* $(C_6H_5)_2S^+\text{-}O^-$, a ratio of 2.6:1. The reaction scheme



gives the steady-state kinetic expression

$$\frac{[(C_2H_5)_2S\text{—}O]}{[(C_6H_5)_2S\text{—}O]} = \frac{2k_2[(C_2H_5)_2S]}{k_3[(C_6H_5)_2S]} + 1$$

Figure 1 is a plot of the kinetic data at 25°, which are well fit by this expression with $k_2/k_3 = 4.0$. The relative reactivities are the same at −78°. Thus the reactive intermediate is 700 times less selective toward the two sulfides than is singlet oxygen.

2. **Intramolecular Reaction.** 1,4-Dithiane, like di-

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(1) Paper XIII: C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, in press. Supported by National Science Foundation Grants GP-8293 and GP-25,790.

(2) C. H. Krauch, D. Hess, and G. O. Schenck, unpublished; quoted by K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(3) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

(4) Also discussed as a possible intermediate in thiophene photooxidation: H. H. Wasserman and W. Strehlow, *Tetrahedron Lett.*, 795 (1970); G. N. Skold and R. H. Schlessinger, *ibid.*, 791 (1970).

(5) Product amounts were determined gas chromatographically using an internal standard and a detector calibrated by weighed amounts of knowns. Rose bengal was used as sensitizer in methanol and acetonitrile and zinc tetraphenylporphine in ether and benzene.