Table I. Cyanosilylation of *p*-Quinones (eq 2)[7]

p-Quinone[a]	Ratio **2**:**3**[b]	% yield[c]	Mp (bp), °C[d]
1a (R_1, R_2, R_3 = H)		80	67–67.5
1b (R_1 = CH_3; R_2, R_3 = H)	89:11	92	(100–102 (0.8 mm))
1c (R_1 = OCH_3; R_2, R_3 = H)[e]	100:0	80	58–60
1d (R_1 = OCH_3; R_2 = H; R_3 = CH_3)[f]	100:0	90	63.5–64
1e (R_1, R_2 = OCH_3; R_3 = H)[g]	100:0	65 (100)	101.8–102
1f (R_1, R_2 = CH_3; R_3 = H)	94:6	(100)	. . .[h]
1g (R_1, R_2 = *t*-Bu; R_3 = H)	0:100	(98)	. . .[h]
1h (R_1 = H; R_2R_3 = C_4H_4)[j]		75	. . .[i]
1i (R_1 = CH_3; R_2R_3 = C_4H_4)[j]	91:9[h]	96	(110–120 (0.1 mm))
1j (R_1 = OCH_3; R_2R_3 = C_4H_4)[j]	100:0	82	72–73

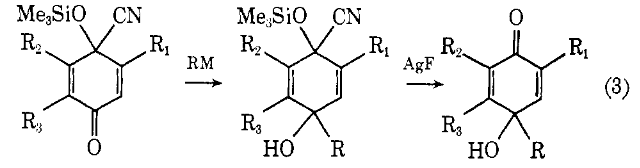
[a] Unless specified, the starting quinone is commercially available. [b] Ratios determined by nmr. [c] Yields in parentheses determined by nmr; all others are of purified adduct. [d] Values in parentheses are boiling point of liquid products. [e] C. de Corral, *Chem. Abstr.*, **52**, 7257*i* (1958). [f] Reference 1c. [g] *Org. React.*, **4**, 343 (1948). [h] Adduct reverts to quinone upon attempted distillation. [i] Product always contaminated with 3–4% naphthoquinone. [j] Notation C_4H_4 refers to fused benzene ring.

Table II. *p*-Quinols from TMSCN-Quinone Adducts (eq 3)[7]

Protected quinone	RM[a]	% yield[b] of **5**	Mp, °C
2a (R_1, R_2, R_3 = H)	CH_3Li	89	76–78[c]
	C_6H_5MgBr	86	105–106.5[d]
	n-C_4H_9Li	75	48–50
	n-C_4H_9MgBr	65	48–50
2c (R_1 = OCH_3; R_2, R_3 = H)	CH_3Li	73	102–104
2d (R_1 = OCH_3; R_2 = H; R_3 = CH_3)	CH_3Li	87	114–115
2f (R_1, R_2 = CH_3; R_3 = H)	CH_3Li	77	37–43[e]
2h (R_1 = H; R_2R_3 = C_4H_4)	CH_3Li	89	103–104
2j (R_1 = OCH_3; R_2R_3 = C_4H_4)	CH_3Li	79	125–126

[a] One equivalent of RM was added to **2** in ether at −70°. [b] Values correspond to purified quinol. [c] F. Wessely and F. Sinwell, *Monatsch. Chem.*, **81**, 1055 (1950); see also ref 15a. [d] Reference 15b. [e] E. Adler, J. Dahlen, and G. Westin, *Acta Chem. Scand.*, **14**, 1580 (1960).

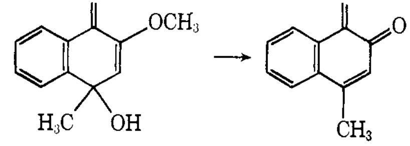
tions on the unprotected quinone carbonyl, a wide variety of otherwise relatively inaccessible compounds can be synthesized in good yield. A simple demonstration of the utility of TMSCN–quinone adducts as effective precursors to *p*-quinols is illustrated (eq 3). In contrast to the behavior of unprotected *p*-quinones,[2] organometallic reagents have been found to undergo clean 1,2 addition to **2** at −70°[12] affording the adducts **4**. These intermediates can then be deblocked to the desired *p*-quinols in high yield with silver fluoride in aqueous tetrahydrofuran (25°). Removal of the TMS-CN blocking group under these conditions is virtually instantaneous. This general synthesis of *p*-quinols is far superior to existing methods.[13] As illustrated in Table II, the two-step conversion of the monoprotected quinones **2** into the *p*-quinols **5** proceeds in good yields.[7]



(3)

2 **4** **5**

With a simple synthesis of *p*-quinols now available, further utilization of these intermediates should be encouraged. For example, TMSCN–quinone adducts **1c–e** and **1j** may serve as useful precursors to substituted *o*-quinones. This is suggested by the fact that quinol **5j** (R = CH_3) may be transformed ($Cu(BF_4)_2$, CH_3CN, 25°) in 85% yield to **7**.[14] On the other hand, *p*-quinols such as **5a** (R = CH_3 or C_6H_5)[15] undergo facile dienone–phenol rearrangement under standard conditions to substituted *p*-hydroquinones.



5j **7**

Applications of this new quinone blocking procedure[16] in the areas of alkaloid and quinone synthesis will be reported in the due course.

Acknowledgment. We wish to thank the Camille and Henry Dreyfus Foundation for unrestricted research support.

D. A. Evans,*[17] J. M. Hoffman, L. K. Truesdale
Contribution No. 3172
Department of Chemistry, University of California, Los Angeles
Los Angeles, California 90024

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(12) Optimum yields of **4** are obtained with 1 equiv of RM in ether at −70°. At this temperature slightly better yields are obtained with the lithium as opposed to the magnesium alkyls.

(13) For an excellent review of methods of preparation of *p*-quinols as well as their reactions see A. J. Waring, *Advan. Alicycl. Chem.*, **1**, 129 (1966).

(14) Compound **7** has been synthesized independently: L. Fieser and C. Bradsher, *J. Amer. Chem. Soc.*, **61**, 417 (1939). This transformation correlates with the structural assignments for both **5j** (R = CH_3) and **2j**.

(15) (a) S. Woodwin and B. Witkop, *ibid.*, **79**, 179 (1957); (b) Y. Abe, *Bull. Chem. Soc. Jap.*, **18**, 93 (1943).

(16) Detailed experimental procedures will be provided upon request.

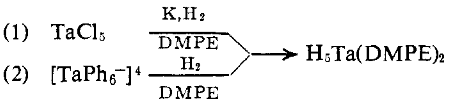
(17) Camille and Henry Dreyfus Teacher–Scholar Recipient (1971–1976); Alfred P. Sloan Fellow (1972–1974).

Synthesis of a Tantalum Pentahydride Complex

Sir:

Phosphine-stabilized polyhydrides are known for transition metals of groups VI–VIII but not for metals of groups IV and V.[1] The synthesis of $H_5Ta(DMPE)_2$ (1) (DMPE = $(CH_3)_2PCH_2CH_2P(CH_3)_2$, 1,2-bisdimethylphosphinoethane) is now reported. This synthesis extends to group V the series of third-row, formally d^0, polyhydrides illustrated by $H_7Re(Ph_2PCH_2CH_2PPh_2)$[2] and $H_6W(PMe_2Ph)_3$.[3]

Compound 1 was synthesized by two routes



1

In reaction 1, a mixture of 1.8 g (5.0 mmol) of $TaCl_5$, 3.8 g (25 mmol) of DMPE, and 2.0 g (51 mmol) of potassium, in 10 ml of benzene, was agitated overnight at 115° in a Hastelloy-C pressure vessel under 1500 psi of hydrogen. After filtration and evaporation of the solvent, the product was crystallized from hexane to yield 0.45 g of **1**. The yields from this type of reaction have varied from 0 to 40%. In reaction 2, a mixture of 54 g (0.058 mol) of $[Li(THF)_4][TaPh_6]$ (THF = tetrahydrofuran), 27 g (0.18 mol) of DMPE, and 250 ml of THF was agitated for 5 hr at 45° in a pressure vessel under 1500 psi of hydrogen. Volatiles were removed from the soluble portion of the reaction mixture and the residue was crystallized from hexane to yield 7.6 g of **1**. An orange THF-insoluble solid, 4.9 g, present in the product mixture is presumably an anionic derivative of **1**. Treatment of a benzene suspension of the solid with 1.2 ml of ethanol produced an additional 2.3 g of **1**. Excess alcohol reduced the yield. Yields from reaction 2 are reproducible, 30–40%. The pentahydride is an air-sensitive white crystalline solid (mp 133–135° dec; mol wt calcd 486, found (cryoscopic in benzene) 464; ir (Nujol) 1544 cm^{-1} (Ta–H stretch)).

The hydride ligands in **1** are readily substituted. Exposure of the pentahydride to hydrogen chloride, water, or ethanol results in rapid generation of hydrogen. Deuterium exchange at the hydride sites (ν_{Ta-D}, 1110 cm^{-1}) occurs when the complex is heated in benzene-d_6 solution at 80° under 900 psi of deuterium. Like $(C_5H_5)_2MH_3$[5] (M = Nb or Ta), **1** catalyzes the exchange of hydrogen with benzene.[6] At 80° in benzene solution under 1500 psi of carbon monoxide, it is converted to the hydridotantalum carbonyl $HTa(CO)_2(DMPE)_2$ (**2**) in 58% yield.[7] (Orange crystals from hexane; mp 140–141°; mol wt calcd 538, found 538 (mass spectrum); ir (C_6D_6 solution) 1737 (C≡O stretch) and 1589 cm^{-1} (Ta–H stretch)). The corresponding deuteride (ν_{Ta-D} = 1137 cm^{-1}), *ca.* 40% enriched, was obtained by a similar procedure from $(H,D)_5Ta(DMPE)_2$.

The compositions and molecular dynamics of **1** and **2** are verified by nmr data.[8] For **1**, the hydride count is obtained from the multiplicity of the ^{31}P spectrum (toluene-d_8, ligand protons noise decoupled, 1:5:10:10:5:1 sextet, 22.4 ppm below 85% H_3PO_4). The hydride nmr spectrum, a 1:4:6:4:1 quintet (C_6D_6, τ 10.70, J_{PH} = 35.0 Hz), is consistent with stereochemical nonrigidity of the molecule over the accessible temperature range ($CHClF_2$, to −140°). Compound **2** is fluxional at 90°, but rigid near 0°.[9]

All of the previously known niobium and tantalum hydride complexes are derivatives of $(\pi\text{-}C_5H_5)_2M$.[10] The cyclopentadienyl ligands formally occupy six of the available coordination sites in these complexes by π bonding[11] and in some cases further deactivate the metal by forming carbon to metal σ bonds as in $[(C_5H_5)(C_5H_4)TaH]_2$.[12] Comparison of the chemistry of the cyclopentadienyl derivatives with the potentially more reactive $(DMPE)_2TaH_5$ is in progress.

Acknowledgments. I thank P. Meakin for the nmr data, N. Schlichter for ir data, and U. Klabunde for permission to quote results prior to publication.

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[1] A recent review is "Transition Metal Hydrides," Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971.

[2] J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).

[3] J. R. Moss and B. L. Shaw, *Chem. Commun.*, 632 (1968).

[4] The synthesis of this new anion by U. Klabunde will be reported separately.

[5] U. Klabunde and G. W. Parshall, *J. Amer. Chem. Soc.*, **94**, 9081 (1972).

[6] U. Klabunde, unpublished results.

[7] Compound **2** has been independently synthesized in the laboratory of J. A. Connor. J. A. Connor, personal communication.

[8] Microanalytical data are: Calcd for $C_{12}H_{37}P_4Ta$ (**1**): C, 29.6; H, 7.7; P, 25.5; Ta, 37.2. Found: C, 29.8; H, 7.8; P, 25.5; Ta, 37.5. Calcd for $C_{14}H_{33}O_2P_4Ta$ (**2**): C, 31.2; H, 6.2. Found: C, 31.2; H, 6.1.

[9] Spectra are analyzed as AA′BB′X systems. A detailed line shape analysis of the permutational process and X-ray diffraction studies of **2** are in progress. P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, to be submitted for publication.

[10] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961); E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5234 (1970); F. N. Tebbe and G. W. Parshall, *ibid.*, **93**, 3793 (1971).

[11] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

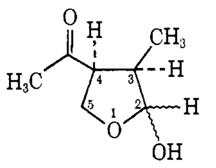
[12] L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973).

Fred N. Tebbe
Contribution No. 2020 from the Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898
Received April 27, 1973

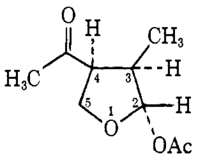
Stereochemistry and Synthesis of the Antileukemic Agent Botryodiplodin

Sir:

In 1968, Arsenault[1] defined the gross structure of an antibiotic isolated from *Botryodiplodia theobromae* Pat.[2] as 2-hydroxy-3-methyl-4-acetyltetrahydrofuran (I) by chemical ionization mass spectrometry. Aside from its antibiotic character, compound I (botryodiplodin) also exhibits antileukemia activity[3] and the interesting property of turning the skin of individuals various shades of pink[2] 2–3 hr after its application.



I



II

Although the nmr of I in CCl_4 was complicated, due to anomers at C_2, the corresponding acetate II appeared to be a single isomer and was tentatively assigned structure II,[1] based on the value of J_{H_3,H_4} (7 Hz). Because of the ambiguity of assigning stereochemistry

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[1] G. P. Arsenault, J. R. Althaus, and P. V. Divekar, *Chem. Commun.*, 1414 (1969).

[2] R. Sen Gupta, R. R. Chandran, and P. V. Divekar, *Indian J. Exp. Biol.*, **4**, 152 (1966).

[3] Results of preliminary testing by the National Institutes of Health.