K_{bo}, and K_{wo} are established as a function of temperature and the extent to which the factor $(1 + K_{w1})/(1 + K_{a1})$, in any particular instance, departs from unity. A more detailed account of these and other considerations will appear elsewhere. However, we consider the present treatment of the temperature dependence of these ionogenic reactions to be more informative than that based on empirical equations which are virtually devoid of theoretical content.

Registry No. Benzoic acid, 65-85-0; water, 7732-18-5.

Preparation and Properties of Sterically Unhindered Cis and Trans Dihydrides of Platinum(II)

Ralph S. Paonessa and William C. Trogler*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received November 9, 1981

Dihydrobis(tertiary phosphine) complexes of platinum(II), PtL_2H_2, undergo a broad spectrum of reactions.[1-17] Examples include insertion,[5-7] dimer formation,[11,12] metallation,[8] formation of platinum(0) compounds,[11,15] oxidative addition,[9,13] and catalysis of the water-gas shift reaction[10] and of alkene hydrogenation.[11] Almost all such dihydrides previously prepared contain bulky tertiary phosphine ligands and assume a trans geometry when L is monodentate. The only known cis dihydrides of this class contain bulky chelating diphosphine ligands.[4,11] In the absence of steric effects, the cis geometry should be electronically favored, since the trans influence of hydride is greater than that of phosphines.[18] The results of a recent ab initio calculation on $Pt(PH_3)_2H_2$ also indicate the cis geometry will be electronically favored.[16]

Previous attempts to prepare platinum(II) dihydrides containing small phosphines have met with limited success, and decomposition often occurs.[1,3,7,11,17] It is generally believed that bulky formation phosphines stabilize" PtL_2H_2 by hindering approach to the PtH_2 moiety.[1,3,11,17] Conversely, analogues which contain small phosphine ligands should be more reactive. We report the synthesis and chemistry of stable but highly reactive unhindered *cis*- and *trans*-PtL_2H_2 complexes and the first examples of cis–trans isomerization of platinum(II) dihydrides. These cis dihydrides are to our knowledge the first examples of four-coordinate d^8 ML_2H_2 in which the cis geometry is not constrained by chelating ligands.

The dihydrides *cis*- and *trans*-PtL_2H_2 (*cis*- and *trans*-**1**, L = PEt_3; *cis*- and *trans*-**2**, L = PMe_3) are readily prepared by bubbling hydrogen (1 atm, 25 °C) through solutions of $PtL_2(C_2H_4)$[19] (reaction 1). These reactions proceed to completion in about 15

$$PtL_2(C_2H_4) + H_2 \rightleftarrows PtL_2H_2 + C_2H_4 \qquad (1)$$

min as ethylene is swept from the system. Ethane was not detected during the reaction by ^1H NMR spectroscopy in solution nor by gas chromatographic analysis of the gas phase. The ratio of cis and trans isomers formed depends on the solvent (vide infra). All the reactions described here can be conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which shows quantitative conversions to products.

The dihydride products are readily identified by examination of their ^1H and ^{31}P NMR spectral parameters (Table I). The ^1H NMR spectrum of each trans-dihydride complex exhibits a hydride resonance which is a 1:2:1 triplet arising from coupling to the two phosphines cis to hydride. The hydride resonance of each cis dihydride complex is a second-order doublet of doublets, arising from coupling of each hydride ligand to a cis phosphorus nucleus and to a trans phosphorus nucleus. The spectral parameters in Table I accord well with those of previously reported cis and trans dihydrides of platinum(II).[1-4,8,11,17,20]

Complexes **1** and **2** isomerize in solution to produce an equilibrium mixture of *cis*- and *trans*-PtL_2H_2 (reaction 2). The

$$trans\text{-}PtL_2H_2 \overset{K}{\rightleftarrows} cis\text{-}PtL_2H_2 \qquad (2)$$

equilibrium constant K depends upon both the solvent and the ligand, L (Table II).[21] Note that, for a given L, the relative concentration of cis isomer increases in going from the nonpolar hydrocarbon solvent to the polar solvent acetone. Since the cis isomer has a dipole moment, it should be better solvated in polar media. Second, in a given solvent, the cis geometry is more favored when L is PMe_3 than when it is PEt_3. Only 3% *cis*-$Pt(PEt_3)_2H_2$ can be detected in toluene, whereas ca. 20% of the PMe_3 dihydride is present in the cis form in this solvent. In acetone *cis*-$Pt(PEt_3)_2H_2$ is still the minor isomer (10%), but upon changing to PMe_3 the cis isomer predominates (70%). Similar results are obtained in other hydrocarbon (benzene) and polar (acetonitrile, methanol, tetrahydrofuran) solvents. These results suggest there is a delicate balance among the steric, electronic, and solvation effects that control the equilibrium between cis and trans isomers.

Analytically pure[22] *trans*-**1** can be isolated as off-white crystals by cooling a concentrated *n*-hexane solution of *trans*-**1** under hydrogen. This hygroscopic solid can be handled briefly in air and is indefinitely stable under 0.5 atm of H_2 at room temperature but decomposes slowly under vacuum. Solutions of **1** under hydrogen in hydrocarbon solvents or in acetone are quite stable. (A

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(1) Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 918–919.

(2) Immirzi, A.; Musco, A.; Carturan, G.; Belluco, U. *Inorg. Chim. Acta* **1975**, *12*, L23–L24.

(3) Leviston, P. G.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1976**, *110*, 271–279.

(4) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1976**, 365–366.

(5) Albinati, A.; Musco, A.; Carturan, G.; Strukel, G. *Inorg. Chim. Acta* **1976**, *18*, 219–223.

(6) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35–L36.

(7) Clark, H. C.; Goel, A. B.; Wong, C. S. *J. Organomet. Chem.* **1978**, *152*, C45–C47.

(8) Clark, H. C.; Goel, A. B.; Goel, R. G.; Ogini, W. O. *J. Organomet. Chem.* **1978**, *157*, C16–C18.

(9) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *J. Chem. Soc., Dalton Trans.* **1978**, 1167–1170.

(10) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941–3942.

(11) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.

(12) Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilson, R. D.; Ibers, J. A.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 2239–2250.

(13) Clark, H. C.; Goel, A. B.; Billard, C. *J. Organomet. Chem.* **1979**, *181*, 431–440.

(14) Ferguson, G.; Siew, P. Y.; Goel, A. B. *J. Chem. Res., Synop.* **1979**, 362–363.

(15) Clark, H. C.; Goel, A. B.; Wong, C. S. *Inorg. Chim. Acta* **1979**, *34*, 159–160.

(16) Kitaura, K.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2891–2892.

(17) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134–2140.

(18) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

(19) We have prepared $PtL_2(C_2H_4)$ (L = PEt_3, PMe_3) by the photochemical reaction $PtL_2(C_2O_4) + C_2H_4 \xrightarrow{h\nu} PtL_2(C_2H_4) + 2CO_2$: Paonessa, R. S.; Trogler, W. C., to be submitted. An alternative route has been described: Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Inorg. Chem.* **1981**, *20*, 1312–1314.

(20) The dihydride *trans*-**1** has been observed previously in solution.[17]

(21) We are confident that we are observing true equilibrium concentrations in solution since (a) the value of K under a given set of conditions is reproducible among several independently prepared samples, (b) the same value of K is obtained either by dissolving a previously prepared sample of PtL_2H_2 in a given solvent or by generating PtL_2H_2 in that solvent [e.g., by reaction of $PtL_2(C_2H_4)$ and H_2], and (c) after reactions which disturb the equilibrium by partially consuming *cis*- and/or *trans*-PtL_2H_2 (e.g., after adding less than a stoichiometric amount of C_2H_4), the cis–trans ratio returns to its equilibrium value. We have not studied the rates of isomerization of **1** and **2** in detail; however, solutions of **1** reach equilibrium within ca. 15 min at 25 °C, and solutions of **2** equilibrate much faster. We do not yet know the mechanism of isomerization of **1** and **2**, and, for example, whether isomerization could be catalyzed by traces of impurities.

(22) Anal. Calc: Pt, 45.01; P, 14.29; C, 33.25; H, 7.44. Found: Pt, 44.98; P, 14.55; C, 32.74; H, 7.21.

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Table I. NMR Parameters of *cis-* and *trans-*PtL_2H_2[a]

		$^{31}P\{^1H\}$ NMR		^1H NMR, hydride			
compd	L	chem shift, ppm[b]	$^1J_{Pt-P}$, Hz	chem shift, ppm	$^1J_{Pt-H}$, Hz	$^2J^{cis}_{P-H}$, Hz	$^2J^{trans}_{P-H}$, Hz
trans-**1**	PEt_3	27.7 s	2764	−2.96 t	790	18	
cis-**1**	PEt_3	18.9 s	1984	−3.56 dd	1030	24	172
trans-**2**	PMe_3	−21.1 s	2594	−2.67 t	807	20	
cis-**2**	PMe_3	−21.7 s	1875	−3.81 dd	1028	24	179

[a] NMR spectra were recorded in acetone-d_6 at −30 °C; s = singlet, t = triplet, dd = doublet of doublets. Couplings to platinum indicate 1:3.9:1 satellites arising from ^{195}Pt (33.8%, $I = 1/2$). [b] Downfield chemical shifts are positive relative to 85% H_3PO_4 at 0 ppm.

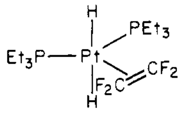
Table II. Equilibrium Constants for *trans*-$PtL_2H_2 \overset{K}{\rightleftarrows}$ *cis*-PtL_2H_2

L	solvent	K	cone angle of L, deg[a]
PEt_3	toluene	0.03	132
	acetone	0.12	
PMe_3	toluene	0.3	118
	acetone	2.2	

[a] Reference 32a.

solution of **1** in C_6D_6 under 0.5 atm of H_2 showed no signs of decomposition after 1 year at room temperature.) Under vacuum, these solutions slowly decompose to yield $Pt(PEt_3)_3$ and platinum metal. A detailed investigation of the chemistry of **1** reveals much greater reactivity than that of more sterically hindered analogues. The reactions described below proceed cleanly under mild conditions (25 °C, 1 atm of gases).

Ligands which are π acceptors such as CO, C_2H_4, and C_2F_4 readily displace H_2 from **1** to produce zero-valent compounds $Pt(PEt_3)_2L_n$ ($L = CO$, $n = 2$; $L = C_2H_4$, C_2F_4, $n = 1$).[23] The reaction of *trans*-**1** with C_2F_4 rapidly produces an intermediate adduct **3**, which loses H_2 over 0.5 h to produce $Pt(PEt_3)_2(C_2F_4)$.[24] Addition of 1 equiv of PEt_3 to a solution of *trans*-**1** in toluene produces the known five-coordinate adduct **4**.[25] The formation of **3** and **4** illustrates the ability of unhindered 16-electron PtL_2H_2 complexes to expand their coordination sphere and form 18-electron species. Similar intermediates may be involved in the reactions of **1** with C_2H_4 and CO.



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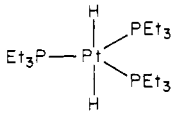

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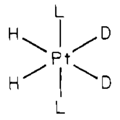
When solutions of **1** in toluene are placed under an atmosphere of D_2, both *trans*-$Pt(PEt_3)_2HD$ and *trans*-$Pt(PEt_3)_2D_2$ form, along with H_2 and HD. If an excess of H_2 and D_2 are present, they are catalytically scrambled to produce an equilibrium mixture of H_2, HD, and D_2.[26] Similarly, Et_3SiH reacts reversibly with **1** to yield *cis*-$Pt(PEt_3)_2H(SiEt_3)$ and H_2. If the reaction is carried out with an excess of Et_3SiH under a D_2 atmosphere, Et_3SiD forms catalytically. The reaction of **1** with methyl iodide immediately produces *trans*-$Pt(PEt_3)_2HI$ and CH_4. It is possible these reactions proceed by oxidative addition to form platinum(IV) intermediates such as **5**, **6**, and **7**; reductive elimination would then lead to the observed products. There is considerable evidence in favor of platinum(IV) intermediates in a host of reactions of platinum(II) compounds containing phosphine ligands.[9,13,27] Alternatively, a bimolecular exchange between platinum centers could account for the H/D exchange reactions. This possibility is also reasonable, in light of the ability of hydride to bridge transition-metal centers,[28] the growing number of dimers of platinum and phosphines bridged by hydrides,[12,29] and the formation of dimers via the dehydrogenation of *cis*-Pt(diphos)H_2.[11] Finally, the possibility of mechanisms involving phosphine dissociation should be considered.[30] Whitesides and co-workers have observed such processes in the decomposition of dialkylbis(phosphine)platinum(II) complexes, albeit under much more extreme conditions than those described here;[31] however, the high trans effect of hydride[18] could promote dissociation of L from *cis*-PtL_2H_2. Careful kinetic and spectroscopic studies will be necessary to identify mechanisms in these very labile systems.



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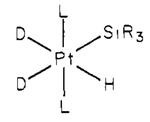

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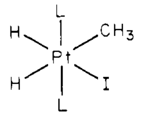

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(23) The reactions of **1** with carbon monoxide or ethylene are complete within minutes, and no hydrogenation products were observed by ^1H NMR spectroscopy. Gas chromatographic analysis of the gas-phase (Molecular Sieve 5X, 6-ft × $^1/_8$-in. o.d., 210 °C) in the reaction with ethylene showed little or no ethane was produced. At much longer times (1 day), ethane was detected above solutions of **1** under 0.5 atm of H_2 + 0.5 atm of C_2H_4; this apparent catalytic hydrogenation is under study.

(24) (a) The geometry of **3** has been inferred from $^{31}P\{^1H\}$, ^1H, ^{19}F NMR, and IR spectroscopic data. The phosphines, hydrides, and fluorines are, respectively, chemically equivalent. $^{31}P\{^1H\}$ NMR δ −6.1 (m, $^1J_{Pt-P} = 1734$ Hz); ^1H NMR (hydride) δ −9.89 (m, $^1J_{Pt-H} = 749$ Hz); ^{19}F NMR δ 20.8 (m, relative to C_2F_4 at 0 ppm). The low value of $^1J_{Pt-P}$ is expected for a pseudo platinum(IV) complex. The complex multiplet patterns in the $^{31}P\{^1H\}$ and ^{19}F NMR spectra very closely resemble those seen in the respective spectra of $Pt(PEt_3)_2(C_2F_4)$; such a result is reasonable if the phosphines and C_2F_4 are also in the same plane in **3**. Finally, the low value of the platinum hydride IR signal ($\nu PtH_2 = 1812$ cm^{-1}) is assignable to the antisymmetric *trans*-H–Pt–H stretch. (b) A number of related platinum(II) adducts have been reported. See, for example: (a) Uguagliati, P.; Baddley, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 5446–5452. (b) Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1970**, *9*, 2670–2675. (c) Ibid. **1971**, *10*, 18–25. (d) Davies, B. W.; Puddephatt, R. J.; Payne, N. C. *Can. J. Chem.* **1972**, *50*, 2276–2284.

(25) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543–3544.

(26) The percentage of HD in the gas phase (determined by gas chromatography) over a stirred benzene solution at 25 °C that contained 1 mol % *trans*-**1** ([*trans*-**1**] = 0.009 M) was monitored as a function of time. Excellent first-order kinetic behavior was observed over three half-lives as the isotopic distribution approached equilibrium. A statistical analysis of the exchange kinetics reveals the turnover number for the degenerate exchange $PtL_2H_2 + H_2 \rightarrow PtL_2H_2 + H_2$ (i.e., the gross exchange rate, regardless of isotope) is 1.6 ± 0.4 min^{-1} at 25 °C. The solutions remain homogeneous, and no induction period is observed; partial decomposition of **1** by introduction of oxygen results in a *decrease* in the rate of exchange. These observations, along with the well-defined kinetic behavior observed and the demonstrated stability of **1** under the mild catalytic conditions, argue against the possibility that the observed catalysis arises from unseen decomposition products.

(27) See, for example: (a) Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: New York, 1974; pp 95–108, 181–183. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 207–208. (c) Halpern, J.; Falk, C. D. *J. Am. Chem. Soc.* **1965**, *87*, 3523–3524. (d) Belluco, U.; Giustiniani, M.; Graziani, M. *Ibid.* **1967**, *89*, 6494–6500. (e) Bentham, J. E.; Cradock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587–593. (f) Eaborn, C.; Pidcock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* **1975**, 809–813. (g) Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808–5815. (h) Blacklaws, J. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877–884.

(28) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145–222.

(29) See, for example; (a) Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Chem. Commun.* **1976**, 671–672. (b) Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155–156. (c) Reference 12.

(30) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867 and references therein.

(31) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.*, **1981**, *103*, 3396–3403 and references therein.

The greatly enhanced reactivity of **1**, when compared to bulkier analogues, is no doubt steric in origin, since the electronic properties of PEt_3 and bulkier trialkylphosphines are quite similar.[32] The small PEt_3 ligand allows easier access to the metal center, expansion of the coordination sphere, and facile interconversion between cis and trans isomers. Preliminary results indicate **2** is even more reactive than **1** and that the cis isomers react more readily than the corresponding trans isomers.

In addition to the reactions described above, **1** and **2** undergo a series of facile, reversible reactions in protic solvents to produce dimeric complexes. These reactions will be described separately.[33]

Acknowledgment. We thank the National Science Foundation (Grants CHE78-01615 and 81-050698) for support of this work and Johnson Matthey, Inc. for a generous loan of platinum.

Registry No. *cis*-**1**, 80581-70-0; *trans*-**1**, 62945-61-3; *cis*-**2**, 80540-35-8; *trans*-**2**, 80581-71-1; **3**, 80540-36-9; **4**, 33937-25-6; $Pt(PEt_3)_2(C_2H_4)$, 76136-93-1; $Pt(PMe_3)_2(C_2H_4)$, 69547-16-6; $Pt(PEt_3)_2(CO)_2$, 76125-09-2; $Pt(PEt_3)_2(C_2F_4)$, 53987-15-8; *cis*-$Pt(PEt_3)_2H(SiEt_3)$, 80540-37-0; *trans*-$Pt(PEt_3)_2HI$, 16971-06-5.

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[32] (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348. (b) Henderson, W. A., Jr.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791–5794.

[33] Paonessa, R. S.; Trogler, W. C., to be submitted.

Indole-2,3-quinodimethan Route to *Aspidosperma* Alkaloids: Synthesis of *dl*-Aspidospermidine

Timothy Gallagher and Philip Magnus*

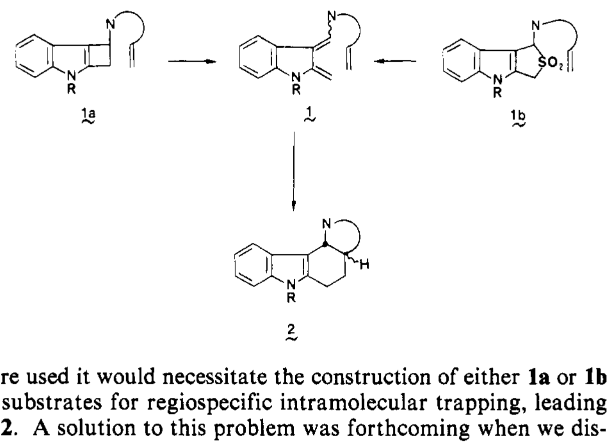
Department of Chemistry, Indiana University
Bloomington, Indiana 47405

John C. Huffman

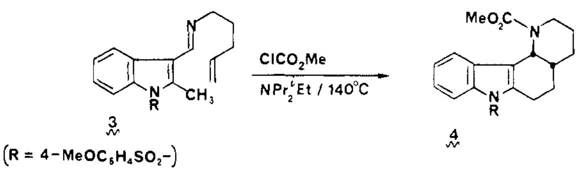
Molecular Structure Center, Department of Chemistry
Indiana University, Bloomington, Indiana 47405

Received November 30, 1981

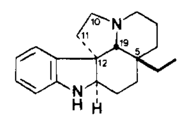
The extension of benzocyclobutene or sulfone precursors of *ortho*-quinodimethanes[1] for the generation of an indole-2,3-quinodimethane, **1**, would be difficult. If classical methodology were used it would necessitate the construction of either **1a** or **1b** as substrates for regiospecific intramolecular trapping, leading to **2**. A solution to this problem was forthcoming when we discovered that the imine **3**, on treatment with methylchloroformate in chlorobenzene at 140 °C, in the presence of diisopropylethylamine, gave the tetracycle **4** in 88% yield.[2]



If this strategy is to be of general use for the synthesis of indole alkaloids, particularly the *Aspidosperma* type **5**, the two-carbon bridge C(10)–C(11) has to be included, and the newly formed ring junction at C(5) must be substituted by an ethyl group. In general the previous strategies employed in *Aspidosperma* alkaloid synthesis have C(10) and C(17) present in a tryptamine system and form the bond C(12)–C(19) to complete the carbon skeleton.[3]



($R = 4\text{-}MeOC_6H_4SO_2\text{-}$)



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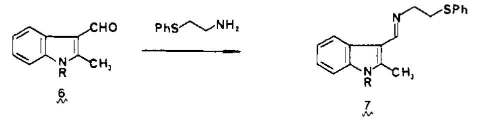
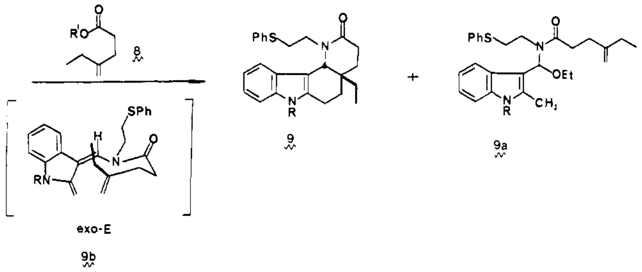
Here we report a straightforward solution to these problems and illustrate this new strategy for indole alkaloid synthesis with the synthesis of *dl*-aspidospermidine **5**.

The 3-formyl-2-methylindole **6**[2] was condensed with 2-(phenylthio)ethylamine[4] to give the imine **7** in quantitative yield. Treatment of **7** with the mixed anhydride **8** ($R^1 = EtO_2C$) derived from 4-ethylpent-4-enoic acid,[5] in chlorobenzene at 140 °C for





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[1] For a review of *ortho*-quinodimethans in synthesis see: Oppolzer, W. *Synthesis* **1978**, 793.

[2] Gallagher, T.; Magnus, P. *Tetrahedron* **1981**, *37*, 3889.

[3] For a general review of indole alkaloid synthesis see: Kutney, J. P. "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley-Interscience: New York, 1977; Vol. 3, p 273. Many synthetic approaches to indole alkaloids have been based on biogenetic proposals: Scott, A. I. *Acc. Chem. Res.* **1970**, *3*, 151. Wenkert, E. *J. Am. Chem. Soc.* **1962**, *84*, 98. Some of these approaches are as follows. (i) Oxindole approach: Ban, Y.; Ohnuma, T.; Nagai, M.; Sendo, Y.; Oishi, T. *Tetrahedron Lett.* **1972**, 5023. Ohnuma, T.; Oishi, T.; Ban, Y.; *J. Chem. Soc., Chem. Commun.* **1973**, 301. Seki, K.; Ohnuma, T.; Oishi, T.; Ban, Y. *Tetrahedron Lett.* **1975**, 723. (ii) Biomimetic syntheses *via* the so-called secodine intermediate: Kuehne, M. E.; Hafter, R. *J. Org. Chem.* **1978**, *43*, 3702. Kuehne, M. E.; Matsko, T. H.; Bohnert, J. C.; Kirkemo, C. L. *Ibid.* **1979**, *44*, 1063; Kuehne, M. E.; Huebner, J. A.; Matsko, T. H.; *Ibid.*, **1979**, *44*, 2477. Kuehne, M. E.; Kirkemo, C. L.; Matsko, T. H.; Bohnert, J. C. *Ibid.* **1980**, *45*, 3259. Ziegler, F. E.; Bennett, G. B. *J. Am. Chem. Soc.* **1971**, *93*, 5930. Ziegler, F. E.; Spitzner, E. B. *Ibid.* **1970**, *92*, 3492. Ziegler, F. E.; Bennett, G. B. *Ibid.* **1973**, *95*, 7458. Ziegler, F. E.; Spitzner, E. B. *Ibid.* **1973**, *95*, 7146. (iii) Nine-membered ring intermediates: Kutney, J. P.; Brown, R. T.; Piers, E.; Hadfield, J. R. *Ibid.* **1970**, *92*, 1708. Kutney, J. P.; Cretney, W. J.; LeQuesne, P.; McKagne, B.; Piers, E. *Ibid.* **1970**, *92*, 1712. Kutney, J. P.; Chan, K. K.; Failli, A.; Fromson, J. M.; Gletsos, C.; Lentwiler, A.; Nelson, V. R.; Pde Souza, J. *Helv. Chim. Acta* **1975**, *58*, 1648. (iv) Rearrangement route: Barton, J. E. D.; Harley-Mason, J. *J. Chem. Soc., Chem. Commun.* **1965**, 298. Harley-Mason, J.; Kaplan, M. *Ibid.* **1967**, 915. For other notable approaches see: Ando, M.; Büchi, G.; Ohnuma, T. *J. Am. Chem. Soc.* **1975**, *97*, 6880. Büchi, G.; Matsumoto, K. E.; Nishimura, H. *Ibid.* **1971**, *93*, 3299. (v) Fischer–Indole approach and various stereochemical points concerning a retro-Mannich/Mannich reaction in the synthesis of aspidospermine and quebrachamine: Stork, G.; Dolfini, J. E. *Ibid.* **1963**, *85*, 2872. Ban, Y.; Sato, Y.; Inoue, I.; Nagai, M.; Oishi, T.; Terashima, M.; Yonemitsu, O.; Kamaoka, Y. *Tetrahedron Lett.* **1965**, 2261. Stevens, R. V.; Fitzpatrick, J. M.; Kaplan, M.; Zimmerman, R. L. *J. Chem. Soc., Chem. Commun.* **1971**, 857. Cordell, G. A. "The Alkaloids"; Vol. XVII, Manske, R. H. F., Rodrigo, R., Ed.; Academic Press: New York, 1979. For approaches that form the C(11)–C(12) bond see: Husson, H.-P.; Thal, C.; Potier, P.; Wenkert, E. *J. Chem. Soc., Chem. Commun.* **1970**, 480. Ziegler, F. E.; Spitzner, E. B. *J. Am. Chem. Soc.* **1973**, *95*, 7146.

[4] Novelli, A.; Zwaig, M. J. *An. Asoc. Quim. Argent.* **1944**, *32*, 82. *Chem. Abstr.* **1945**, *39*, 1409.

0002-7863/82/1504-1140$01.25/0