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.

(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*

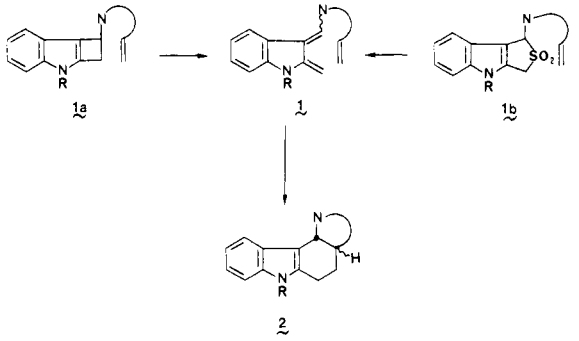
*Department of Chemistry, Indiana University Bloomington, Indiana 47405*

John C. Huffman

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

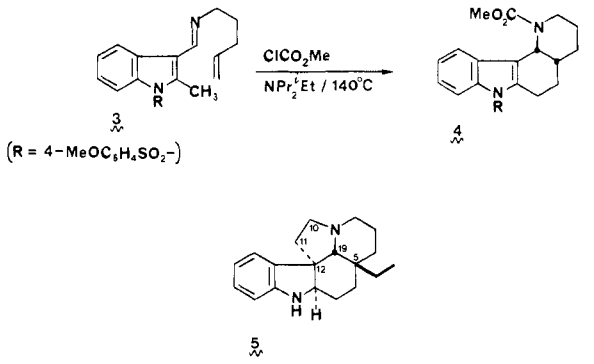
*Received November 30, 1981*

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]

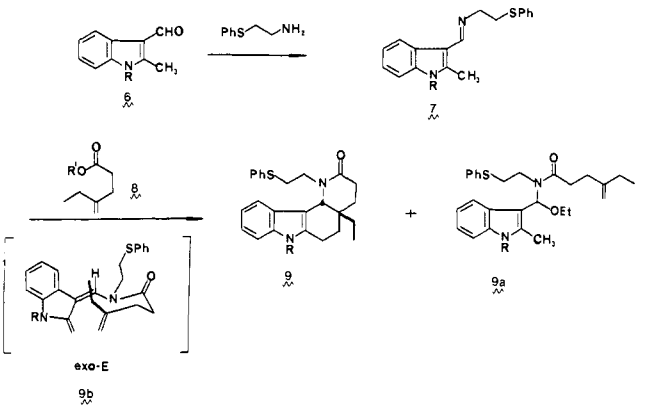
If this strategy is to be of general use for the synthesis of indole alkaloids, particularly the *Aspidosperma* type **5**, the two-carbon bridge C(10)-C(11) has to be included, and the newly formed ring junction at C(5) must be substituted by an ethyl group. In



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]

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



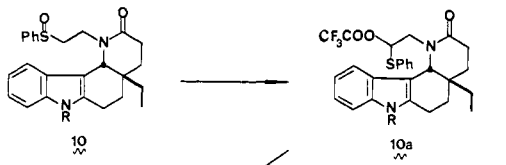
(1) For a review of *ortho*-quinodimethans in synthesis see: Oppolzer, W. *Synthesis* **1978**, 793.
(2) Gallagher, T.; Magnus, P. *Tetrahedron* **1981**, *37*, 3889.

(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 

2.75 h gave the tetracyclic system **9**, mp 195–195.5 °C, in 33% yield after chromatography and crystallization from benzene/hexane. The only other product isolated from this reaction was **9a**, which did not convert into **9** on further heating.[6] The relative stereochemistry of **9** was demonstrated by single-crystal X-ray crystallography to be cis.[7] No trace of any other stereoisomers could be detected in the above reaction mixture. A plausible transition state for this reaction is **9b**.[2] The conformation of **9** in the crystalline state is most unusual, in that the $PhSCH_2CH_2$ group is bent back across the indole ring with the C(11) carbon atom in close proximity to C(12).

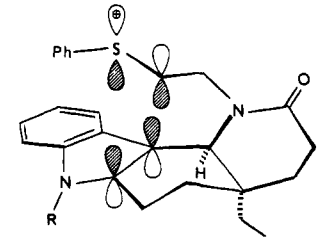
Oxidation of **9** with $MCPBA/CH_2Cl_2/NaHCO_3$ at 0 °C gave the sulfoxide **10** as a mixture of diastereomers in 97% yield. When



10 10a

11 12

the sulfoxides **10** were treated with trifluoroacetic anhydride[8] in dichloromethane at 0 °C for 10 min, the trifluoroacetate **10a** was formed. The mixture was warmed to 20 °C, and chlorobenzene was added and heated at 130 °C for 2.5 h to give the pentacycle **11** in 81% yield after direct crystallization from the reaction mixture, mp 135–137 °C. The structure and stereochemistry of **11** was confirmed by single-crystal X-ray crystallography.[9] The configuration of the PhS group at C(11) was predicted from the conformation of **9**, leading to the sulfonium ion **11a** and its subsequent closure to **11**. Desulfurization of **11** with Raney nickel (W-2, not deactivated) in ethanol at 20 °C for 1 h gave **12** (81%), mp 195–196 °C. Reduction of **12** with $LiAlH_4/THF$ at 20 °C for 48 h cleanly gave *dl*-aspidospermidine **5** (54%), mp 99–103 °C (from acetone).[10,11]



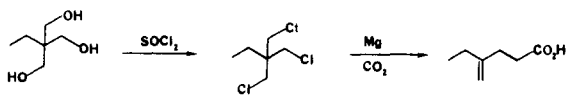
11a

This new strategy for indole alkaloid synthesis provides a short, highly convergent route to aspidospermidine **5** (11.7% overall yield from **6**) and illustrates for the first time the use of an indole-2,3-quinodimethane in synthesis. We anticipate that its flexibility in allowing more complex alkaloids to be readily synthesized through intermediates such as **11**, where C(11), C(8), and C(13) are functionalized, will prove to be its most useful asset.

**Acknowledgment.** The National Institute of Health and Upjohn Co. are gratefully thanked for their support of this work. Professor Martin Kuehne is thanked for the generous gift of (+)-vincadifformine.

**Supplementary Material Available:** ORTEP structures for **9** and **11** and listings of IR, NMR, and microanalytical data (3 pages). Ordering information is given on any current masthead page.

(5) 4-Ethylpent-4-enoic acid was prepared as follows: McCaffery, E. L.; Shalaby, S. W. *J. Organomet. Chem.* **1967**, *8*, 17.



(6) A variety of mixed anhydrides and different activated esters were examined without any improvement in yield. It should be noted that the cyclization reaction **7** → **9** in the desethyl series proceeds in ca. 70% yield at almost the same rate. A detailed description of this reaction will be presented later.

(7) Compound **9** crystallizes in space group $P\bar{1}$ with cell dimensions (at −160 °C) $a$ = 20.992 (13) Å, $b$ = 15.246 (8) Å, $c$ = 10.010 (5) Å, $\alpha$ = 118.83 (2)°, $\beta$ = 92.29 (2)°, and $\gamma$ = 95.22 (2)°. The calculated density for $Z$ = 4 is 1.372 g cm$^{-3}$. A description of the diffractometer, low-temperature apparatus, and data handling techniques are described in: *Inorg. Chem.* **1980**, *19*, 2755. Final residuals for the full-matrix refinement were $R_F$ = 0.097 and $R_{wF}$ = 0.083 for 7312 independent reflections. The two independent molecules in the crystal adapt essentially the same conformation. Complete crystallographic data are available in microfiche form from the Chemistry Library, Indiana University; request IUMSC Report No. 81064.

(8) Pummerer reaction applied to indoles: Oikawa, Y.; Yonemitsu, O. *J. Org. Chem.* **1976**, *41*, 1118.

(9) Compound **11** crystallizes in space group $P\bar{1}$ with cell dimensions (at −160 °C) $a$ = 11.162 (3) Å, $b$ = 15.860 (5) Å, $c$ = 9.321 (2) Å, $\alpha$ = 81.25 (1)°, $\beta$ = 103.63 (1)°, and $\gamma$ = 107.89 (1)°. The calculated density for $Z$ = 2 plus one molecule of benzene solvent in the cell is 1.336 g cm$^{-3}$. Final residuals for the 3946 unique data are $R_F$ = 0.066 and $R_{wF}$ = 0.061. See ref 7 concerning experimental details. Complete crystallographic data are available in microfische form from the Chemistry Library, Indiana University; request IUMSC Report No. 81065.

(10) Djerassi, C.; Budzikiewicz, H.; Wilson, J. M.; Gosset, J.; LeMen, J.; Janot, M.-M. *Tetrahedron Lett.* **1962**, 235. Smith, G. F.; Wahid, M. A. *J. Chem. Soc.* **1963**, 4002. (+)-Vincadifformine was converted into aspidospermidine by decarboxylation to dehydro aspidospermidine followed by reaction with $LiAlH_4$.

(11) The synthetic material was identical [IR (soln), NMR (220 MHz), four TLC systems (20% MeOH/80% EtOAc; 30% $CH_2Cl_2$/70% $Me_2CO$; 40% EtOH/60% EtOAc; 5% MeOH/95% MeCN on silica gel 60F-254)] with the natural material. A wide variation in melting points for racemic aspidospermidine has been observed.

## Highly Reduced Organometallics. 6.[1] Synthesis and Chemistry of Tricarbonylphosphineferrates(2−), $Fe(CO)_3PR_3^{2-}$

Yu-Sen Chen and John E. Ellis*

*Department of Chemistry, University of Minnesota Minneapolis, Minnesota 55455*

*Received November 23, 1981*

Mononuclear carbonylmetallate dianions are well-established species[2] and have been valuable stoichiometric reagents in organic chemistry,[3] metal cluster synthesis,[4] and in the preparation of novel mononuclear organometallic compounds.[2] However, there have been no previous reports on phosphine-substituted metal carbonyl dianions.[5] Since these materials may be as useful in synthetic chemistry as the parent carbonyl dianions, we have recently investigated possible methods for their synthesis. In this paper some of our results are presented, including a potentially general two-step synthesis of carbonylphosphinemetallate dianions.

One-step reductions of $M(CO)_xPR_3$ to $M(CO)_{x-1}PR_3^{2-}$ almost invariably fail since the coordinated phosphine is generally lost in the presence of reducing agents.[6,7] For example, treatment

(1) Part 5: Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6106.
(2) For a review, see: Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.
(3) Collman, J. P., *Acc. Chem. Res.* **1975**, *8*, 342.
(4) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.
(5) Excepted are the completely substiuted $M(PF_3)_4^{2-}$ (M = Fe, Ru, and Os) prepared over 10 years ago: Kruck, T. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 679.

0002-7863/82/1504-1141$01.25/0 