in donor bonding to iron therefore leaves the P-P distance essentially unchanged, which suggests that the lone-pair involvement in P-P bonding is minimal. The remaining interatomic distances and angles within the molecule are normal.

NMR data are as follows: ^{31}P NMR ($CDCl_3$) δ 384.55 (s from 21 to -60 °C (relative to external 85% H_3PO_4)); ^{13}C NMR ($CDCl_3$) SiC_3 (s, δ 1.72), $CHSi_2$ (t, δ 32.1, $J_{N(PC)}$ = 19.5 Hz), CO (s, δ 214.8); ^1H NMR ($CDCl_3$) $SiMe_3$ (s, δ 0.28), CH (br s, δ 3.5); ^{13}C and ^1H NMR shifts are relative to Me_4Si. Both the ^{31}P and ^{13}C NMR spectra are consistent with the structure established by X-ray diffraction. The triplet seen at 32.1 ppm in the ^{13}C NMR for $CHSi_2$ appears to be characteristic of a P-P-containing system and is similar to that observed by Cowley and co-workers for CSi_3 in $(Me_3Si)_3CPPC(SiMe_3)_3$[4] and by others in alkylated diphosphines.[9] In the case of the ^1H NMR, studies are still in progress owing to the unusual behavior of the hydrogen attached to the α-carbon atom. The resonance position is very solvent dependent, and the broad pattern seen at 21 °C is split into a multiplet at low temperature. Clearly the proton is showing dynamic behavior, and variable-temperature NMR (both ^1H and ^{13}C) may explain the unusual behavior; UV-vis ($CDCl_3$) λ_{max} 382 and 287 (sh) nm; IR ν_{CO}(Nujol) 2053 (sh, m), 1988 (sh, m), 1962 cm^{-1}; IR $\nu_{CO}(CH_2Cl_2)$ 2026 (m), 1985 (m), 1953 cm^{-1}.

The extension of this work to other transition metals with a variety of substituents and group 5b metal centers is in progress.

Acknowledgment. We are grateful to the Research Corp. and the NSF (CHE-8116355) for generous financial support. We thank B. Murray and Dr. G. B. Matson for experimental assistance.

Supplementary Material Available: Listing of atom coordinates, temperature factors, bond distances and angles (2 pages). Ordering information is given on any current masthead page.

(10) **Note Added in Proof**: Professor Cowley has informed us that the structure of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ consists of two crystallographically independent molecules with P-P distances of 2.014 (6) and 2.004 (6) Å.

Synthesis of (±)-Kopsanone and (±)-10,22-Dioxokopsane, Heptacyclic Indole Alkaloids

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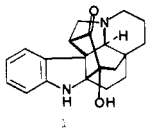
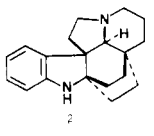
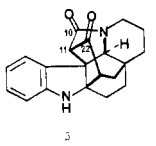
The first documented isolation of a member of the heptacyclic *Aspidofractinine* indole alkaloids was kopsine **1**, in 1890.[1] It was

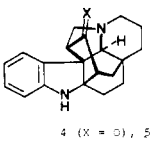






not until the early 1960s that the extraordinary complex cage structure of the kopsane alkaloids was elucidated.[2] It is historically interesting to note that the more famous heptacyclic indole alkaloid strychnine eventually submitted to classical structure elucidation by chemical degradation, whereas the kopsanes did not. Their structures were deduced by mass spectrometry,[3] and subsequently (-)-kopsanone methiodide was confirmed by single-crystal X-ray crystallography.[4] While the hexacyclic indole alkaloid aspidofractinine **2** has been synthesized,[5] there is no literature that describes any synthetic approaches to the more condensed kopsane alkaloids.

The complete synthesis of both 10,22-dioxokopsane **3** and kopsanone **4**, central members of this group of alkaloids, is described in Scheme I. Conversion of the aldehyde **6** into the sulfoxide **10** proceeded by using our previously described methodology.[6] Treatment of **10** with TFAA/0-130 °C gave directly the required homoannular diene **11**.

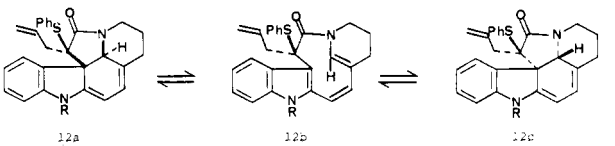


4 (X = O), 5 (X = H,OH)

The formation of the C_{11}-C_{12} bond (**10** → **11**) must procede the elimination of HCl, since we know that the 1,4-dihydrocarbazole that would result from prior elimination of HCl aromatizes (1,4-elimination) to a carbazole under the conditions of this reaction.[7] Consequently, **10** must, via a sulfonium ion (Pummerer reaction), give **10a**, which places the equatorial Cl atom allylic to the newly formed *N-p*-methoxyphenylsulfonyl enamine, thus facilitating its elimination, followed by proton loss to give the homoannular diene **11**.

The crucial allylation at C_{11} was conducted by treatment of **11** with $KN(SiMe_3)_2$/THF/0 °C/allyl bromide, to give *exclusively* **12** (91%), with the stereochemistry shown.

The stereochemical analysis of the alkylation of **11**, at C_{11}, would predict that the incoming electrophile should approach the C-11 carbanion from the convex face to give **12a**. This would



12a 12b 12c

place the allyl group (dienophile) on the wrong face of **11** to undergo [2 + 4] cycloaddition to the ring-C diene. Fortunately, this would not be incompatible with the synthetic plan, since thermal equilibriation (diene ⇄ triene, **12a**/**12b**) provides a pathway to **12c** (mirror image of **12**), which can now cyclize to the heptacyclic kopsane structure **13**. Alternatively the carbanion at C_{11} is pyramidally stable and not delocalized into the amide carbonyl group. Delocalization of negative charge into the amide carbonyl group destroys the amide resonance (ca. 12 kcal mol^{-1}) and may not be necessary since the inductive effect of both the SPh and $CONR_2$ groups is sufficient to stabilize the C_{11} carbanion.

(1) Greshoff, M. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3537.

(2) Bycroft, B. W.; Schumann, D.; Patel, M. B.; Schmid, H. *Helv. Chim. Acta* **1964**, *47*, 1147. Schumann, D.; Bycroft, B. W.; Schmid, H. *Experientia* **1964**, *20*, 202. Kump, C.; Dugan, J. J.; Schmid, H. *Helv. Chim. Acta* **1966**, *49*, 1237. Kump, C.; Schmid, H. *Ibid.* **1962**, *45*, 1090. Battersby, A. R.; Gregory, H. *J. Chem. Soc.* **1963**, 22.

(3) Achenbach, H.; Biemann, K. *J. Am. Chem. Soc.* **1965**, *87*, 4944. Djerassi, C.; Budzikiewicz, H.; Owellen, R. J.; Wilson, J. M.; Kump, W. G.; LeCount, D. J.; Battersby, A. R.; Schmid, H. *Helv. Chim. Acta* **1963**, *46*, 742.

(4) Craven, B. M.; Gilbert, B.; Paes Leme, L. A. *Chem. Commun.* **1968**, 955; see also *J. Chem. Soc. C* **1966**, 1260.

(5) Ban, Y.; Honma, Y.; Oishi, T. *Tetrahedron Lett.* **1976**, *1111*. A biosynthetic route to the aspidofractinine (hexacyclic) alkaloids was proposed: Wenkert, E. *J. Am. Chem. Soc.* **1962**, *84*, 98. Experimental evidence for this proposal was provided: Schnoes, H. K.; Biemann, K. *Ibid.* **1964**, *86*, 5693. For a synthesis of 19-hydroxyaspidofractinine see: Cartier, D.; Patigny, D.; Lévy, J. *Tetrahedron Lett.* **1982**, *23*, 1897.

(6) For a description of this type of cyclization reaction see: Gallagher, T.; Magnus, P. *Tetrahedron*, **1981**, 3889; *J. Am. Chem. Soc.* **1982**, *104*, 1140. The *Z* isomer gave extremely low yields (ca. 10%) of the tetracyclic trans-(axial) chloro isomer.

(7) Exon, C.; Gallagher, T.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1982**, 613.

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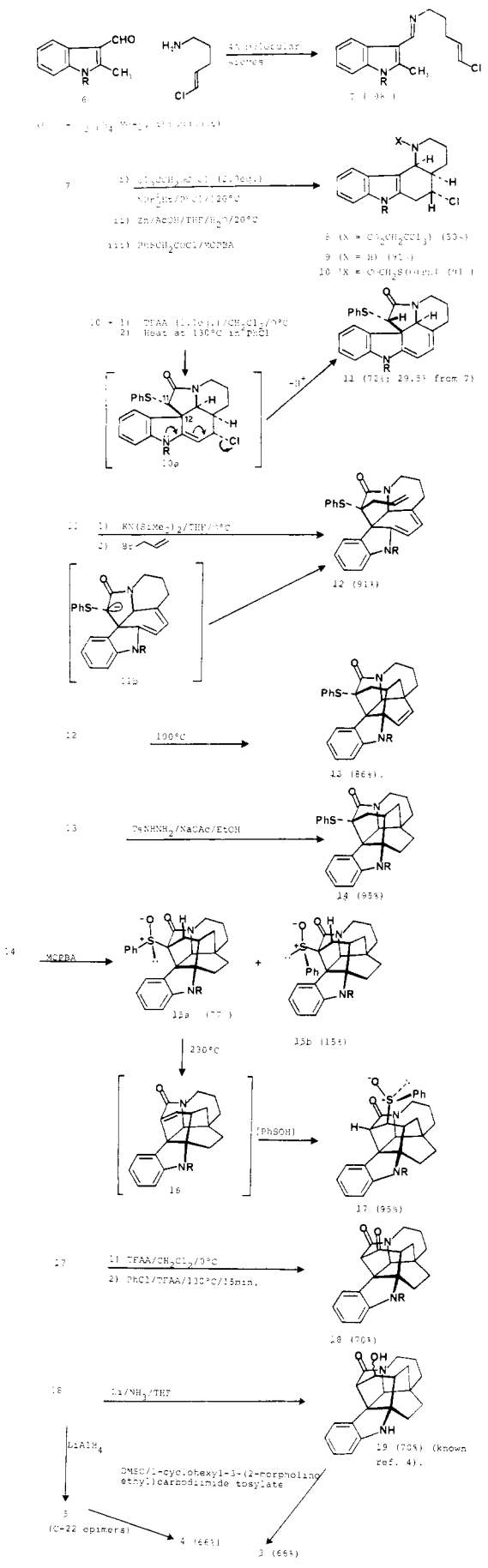
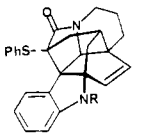
Scheme I



It should be noted that the conversion of **11** into **12** (retention of configuration at C_{11}) does not formally preclude the C_{11} inversion pathway **12a** → **12c** but does imply that the activation energy for **12a** → **12c** must be less than **12/12c** → **13**.[8]

In **12** the allyl group sits directly above the diene, and heating to 100 °C (or melting) cleanly gave the basic heptacyclic kopsane skeleton **13**. It was important to unambiguously confirm this structure (X-ray) since **12** could have cyclized to the fruticosane skeleton **13a**.



13a

Diimide reduction of **13**[9] and oxidation with MCPBA gave a mixture of sulfoxides **15a** (77%) and **15b** (15%). Only one of the two sulfoxides, **15a**, can undergo syn elimination, since the epimer **15b** would have to adopt a conformation that forces the PhS(O) group into the indoline ring. The syn elimination of **15a** required temperatures of 230 °C (3 h; cf. usual conditions, ca. 120 °C)[10] to give, presumably, the torsionally strained α,β-unsaturated amide **16**. The in situ liberated phenylsulfenic acid adds to the α,β-unsaturated amide **16** in a cis addition to give the new sulfoxide **17** as a single epimer at sulfur.[11] The elimination–addition process, in effect, moves the PhS(O) functionality one carbon atom from C-11 to C-22.

Conversion of **17** into **18** utilizing a second Pummerer reaction proceeded in 70% yield. Reduction of **18** was carried out by using either Li/NH_3 or $LiAlH_4$ to give **19** and **5**, respectively. Modified Moffatt oxidation of **19** gave (±)-10,22-dioxokopsane **3**. Similarly oxidation of **5** gave (±)-kopsanone **4**. (Both **3** and **4** were compared with authentic samples: IR, NMR, MS, TLC.)

In conclusion, the route described in Scheme I provides **3** in 14 steps in overall 5.8% yield.[12]

Acknowledgment. The National Institutes of Health (GM 29801) are gratefully thanked for their financial support. The National Science Foundation (CHE 81-05004) are thanked for funds to purchase a 360-H NMR spectrometer. Professor Manfred Hesse (University of Zurich) is thanked for samples of 10,22-dioxokopsane **3** and kopsanone **4** from the collection of the late Professor Hans Schmid. Professor K. Biemann is thanked for the MS comparison. Dr. J. C. Huffman is thanked for X-ray structural determinations of **12** and **13**.

(8) While the diene/triene **12a/12b** interconversion exists as a formal possibility, with many literature analogies; see: Marvell, E. N. "Thermal Electrocyclic Reaction"; Academic Press: New York, 1980; pp 260–305. The energetics of such a process, by comparison with literature data, would suggest that at 25 °C the equilibrium would be overwhelmingly on the side of the diene and that cycloreversion would not occur. For example, cyclononatriene at room temperature (all cis form) gave *cis*-bicyclo[4.3.0]nonadiene: Vogel, E.; Grimme, W.; Dinne, E. *Tetrahedron Lett.* **1965**, 391. Glass, D. S.; Watthey, J. W. H.; Winstein, S. *Ibid.* **1965**, 377. At this stage we cannot formally exclude the diene/triene interconversion; it appears unlikely under the conditions used to make **12**. We intend to examine this point in detail later.

(9) Hart, D. J.; Kanai, K. *J. Org. Chem.* **1982**, *47*, 1555. Sumagawa, M.; Katsube, J. Abstracts of Papers; 7th Symposium on Progress in Organic Reactions and Synthesis; Gifu, Japan, 1980; p 52.

(10) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, **98**, 4887. The epimeric sulfoxide **15b** can be recycled by reduction and oxidation. We are examining its acid-catalyzed epimerization.

(11) Block, E. *J. Am. Chem. Soc.* **1972**, *94*, 642. Jones, D. N.; Lewton, D. A. *J. Chem. Soc., Chem. Commun.* **1974**, 457. The torsionally strained α,β-unsaturated amide **16** (anti-Bredt) would be expected to be extremely susceptible to nucleophilic addition. For a review of bridgehead olefins see: Keese, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528. House, H. O.; Outcalt, R. J.; Cliffton, M. D. *J. Org. Chem.* **1982**, *47*, 2413.

(12) Both synthetic **3** and **4** give very characteristic thin-layer chromatographic responses, identical with authentic samples. 360-MHz NMR spectra confirmed their identity, as did IR spectra when compared to the spectra obtained from authentic samples. Compounds **8**, **9**, **11–14**, **15a/b**, **17**, and **18** gave satisfactory microanalytical data and other spectral determination. The structures of **12** and **13** were determined by single-crystal X-ray crystallography.