the rhoeadine alkaloids.[2] In this manner the alkaloids (±)-cis-alpinine (1) and (±)-cis-alpinigenine (2) have been synthesized without the necessity of preforming a 1,2,3,4-substituted benzene precursor for rings C/D, usually a tedious and low-yielding operation.[3,4]

The synthesis of the indanone 3, achieved by standard methods, will be detailed elsewhere. Thus N-acetyl-homoveratrylamine 4 was successively N-methylated (sodium hydride–methyl iodide in tetrahydrofuran–dimethylformamide) to 5, chloromethylated[5] (formaldehyde–dry hydrogen chloride) to 6, converted to the nitrile 7 (sodium cyanide–dimethyl sulfoxide), and condensed with 2,3-dimethoxybenzaldehyde under base catalysis to the stilbene which was reduced directly (2% sodium amalgam in ethanol) to 8. The nitrile was successively hydrolyzed (ethanolic hydrogen chloride) to the ester 9 and the acid 10 (brief treatment with 5% methanolic potassium hydroxide). Friedel–Crafts cyclization of the acid chloride 11 (aluminum chloride–nitrobenzene) produced the desired indanone 3. The yields in each step of the above sequence were 70% or better, and the properties of all compounds were consistent with the assigned structures.

Base hydrolysis of 3 (10% potassium hydroxide in 50% aqueous ethanol under reflux for 20 hr) produced the indene 12 (62% yield, mp 133–134°) which possessed the 3-benzazepine moiety characteristic of the rhoeadine alkaloids, fused in the correct manner to a potential CD system with the desired substitution pattern. The indene 12 was identical with a rearrangement product of a tetramethoxyspirobenzylisoquinoline[3b] which had been assigned the same structure on the basis of its spectroscopic properties. This provided an independent verification of our synthesis at this stage and unequivocally established the structure of the rearrangement product.

Base-catalyzed oxidation of compound 12 (Triton B in pyridine–molecular oxygen) produced the bright red indenone 13 (79% yield; mp 159–161°, $\nu_{max}^{CHCl_3}$ 1700 cm^{-1}; λ_{max}^{EtOH} 225 (sh), 242 (sh), 308 (sh), 319, and 503 nm; ϵ_{max} 15,400, 15,800, 18,800, 19,300, and 4100, respectively; δ(CDCl$_3$) 2.8–3.1 (m, 2H), 3.6–3.9 (m, 2H), 3.40 (s, 3H), 3.97, 4.04 (s, 2 × 3H), 3.84 (s, 6H), 6.62, 7.93 (s, 2 × 1H), 6.73 and 7.13 (q, 2H, J_{AB} = 8 Hz); M^+ = 381) which on Rose Bengal sensitized photooxidation yielded inter alia the ketolactone 14 analogous to those described earlier[4] (37% yield; mp 214–215°; $\nu_{max}^{CHCl_3}$ 1767 and 1690 cm^{-1}; λ_{max}^{EtOH} 223, 240 (sh), 284 and 321 nm; ϵ_{max} 22,600, 18,300, 11,300, and 14,000, respectively; δ(CDCl$_3$) 2.37 (s, 3H), 3.0–3.6 (m, 4H), 3.80, 3.93, 3.98, 4.17 (s, 4 × 3H), 6.77, 6.97 (s, 2 × 1H), 6.98 and 7.19 (q, 2H, J_{AB} = 8 Hz); M^+ = 413). A systematic examination of this reaction is now underway; in particular it is envisaged that the yields may be improved, the by-products identified, and the

scope defined. Other oxidative methods are available in principle for achieving an equivalent transformation (13 → 14) and these possibilities are being explored.

Sodium borohydride reduction of 14 followed by dilute hydrochloric acid treatment yielded the cis-lactone[4b] 15 (90% yield; mp 195–196°; $\nu_{max}^{CHCl_3}$ 1735 cm^{-1}; λ_{max}^{EtOH} 221, 237 (sh), 287, and 308 nm; ϵ_{max} 23,100, 20,100, 8600, and 5800, respectively; δ(CDCl$_3$) 2.20 (s, 3H), 3.35 and 5.23 (br s, J = <1 Hz), 3.82, 3.88, 3.92, 4.02 (s, 4 × 3H), 6.72, 6.75 (s, 2 × 1H), 7.05 and 7.07 (q, 2H, J = 9 Hz); M^+ = 399). The lactone was reduced with diisobutylaluminum hydride in toluene to the lactol 2 (94% yield; mp 183–184°; λ_{max}^{EtOH} 239 and 282 nm; ϵ_{max} 5800 and 5400, respectively; δ(CDCl$_3$) 2.20 (s, 3H), 3.13 and 4.59 (br s, J = <1 Hz), 3.80, 3.91 (s, 2 × 3H), 3.89 (s, 6H), 6.40 (s, 1H), 6.88 (s, 2H), 6.69 (s, 2H)) which was stable to refluxing 0.25 N hydrochloric acid (3 hr) and is therefore (±)-cis-alpinigenine 2, with the relative configuration[2,6] as shown. Its pmr spectrum and tlc behavior were identical with those of an authentic sample of (+)-cis-alpinigenine.[6] This was methylated with methanolic hydrogen chloride in the usual manner[7] to (±)-cis-alpinine 1 which resisted crystallization. The pmr spectrum of 1 was identical with published data[6] for the compound and the mass spectra of 1 and 2 were virtually identical with published spectra[8] of (+)-alpinine and (+)-alpinigenine, respectively. 1 was converted to a crystalline methiodide (mp 207–208°) which provided satisfactory analytical figures.[9]

This synthetic scheme is not only a valid model for the preparation of the other cis-fused rhoeadine alkaloids[10] but also promises to lead to alkaloids of the spirobenzylisoquinoline (from 3) and phthalideisoquinoline (from 14[4b]) types.

(6) H. Rönsch, Tetrahedron Lett., 4431 (1972). We thank Professor Rönsch for a copy of the pmr spectrum of (+)cis-alpinigenine and for 3.7 mg of the alkaloid.

(7) J. Slavik, L. Dolejš, L. Vokáč, and V. Hanuš, Collect. Czech. Chem. Commun., 30, 2864 (1965).

(8) M. Maturová, H. Potůšilová, F. Šantavý, A. D. Cross, V. Hanuš, and L. Dolejš, Collect. Czech. Chem. Commun., 32, 419 (1967).

(9) Satisfactory elemental analyses were obtained for compounds 2–15.

(10) M. Shamma and L. Töke, Chem. Commun., 740 (1973), have reported the synthesis of an N-benzoylated trans-rhoeadine system.

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(2) For reviews see (a) F. Šantavý, Alkaloids, 12, 398 (1970); (b) M. Shamma, "The Isoquinoline Alkaloids: Chemistry and Pharmacology," Academic Press, New York, N. Y., 1972, p 399.

(3) Two previous syntheses of rhoeadine alkaloids have been achieved by rearrangements of alkaloidal materials. See (a) H. Irie, S. Tani, and H. Yamane, Chem. Commun., 1713 (1970); (b) J. Chem. Soc., Perkin Trans. 1, 2986 (1972).

(4) (a) W. Klötzer, S. Teitel, J. F. Blount, and A. Brossi, J. Amer. Chem. Soc., 93, 4321 (1971); (b) Monatsh. Chem., 103, 435 (1972); (c) W. Klötzer, S. Teitel, and A. Brossi, Helv. Chim. Acta, 54, 2057 (1971), ibid., 55, 2228 (1972).

(5) B. Pecherer, R. C. Sunbury, and A. Brossi, J. Heterocycl. Chem., 9, 609 (1972).

Reactions of Molybdenum and Tungsten Atoms. Syntheses of Bisarene Sandwich Compounds

Sir:

Benzene sandwich compounds of molybdenum and tungsten have been reported by Fischer, Scherer, and Stahl,[1] and prepared by reduction of metal salts with aluminum–aluminum chloride in the presence of ben-

(1) E. O. Fischer, F. Scherer, and H. O. Stahl, Chem. Ber., 93, 2065 (1960).

Table I

Compound	Nmr absorptions (τ)[a]	Compound	Nmr absorptions (τ)[a]
W(benzene)₂	5.00 s		
W(toluene)₂	5.10 s (5.00 H)	Mo(N,N-dimethylaniline)₂	5.42 m (5.02 H)
	8.03 s (3.00 H)		7.76 s (5.97 H)
W(o-xylene)₂	5.18 br s (4.00 H)	Mo(toluene)₂	5.40 m (4.97 H)
	8.09 s (6.26 H)		8.11 s (3.00 H)[b]
W(anisole)₂	4.71 d (2.00 H)	Mo(benzene)₂	5.40 s
	5.24 t (2.00 H)	Mo(fluorobenzene)₂	4.88 d (2.01 H)
	5.72 m (0.93 H)		5.62 t (2.06 H)
	6.88 s (3.30 H)		5.95 m (0.93 H)
W(fluorobenzene)₂	4.50 d (1.75 H)	Mo(chlorobenzene)₂	4.92 d (2.01H)
	5.38 t (2.00 H)		5.57 t (2.11H)
	6.00 m (1.00 H)		5.78 m (0.82H)
Mc(anisole)₂	5.04 d (2.00 H)	Mo(methylbenzoate)₂	4.40 d (1.86 H)
	5.48 t (2.32 H)		5.33 m (3.12 H)
	5.77 m (1.03 H)		6.44 s (3.02 H)
	6.82 s (3.22 H)		

[a] In perdeuteriobenzene or toluene. [b] M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 301 (1973).

zene, 71% yield for molybdenum and 1.8% for tungsten. At best this method is applicable to benzene and alkyl benzenes.

A more versatile method is the interaction of the free metal atoms with the substrates. The recent report by Green[2] and coworkers of the reaction of molybdenum atoms with benzene, to produce dibenzenemolybdenum, prompts us to report our results in synthesizing a variety of sandwich compounds with both molybdenum and tungsten atoms.

Green and coworkers employed e-gun heating of a molybdenum target for vaporization. We had dropped that method in favor of a simpler, less costly, and cleaner method, vaporization by resistive heating of tungsten or molybdenum wires, an extension of the methods employed for carbon vaporizations.[3] The 5–7 kV electron beam employed in e-gun methods can be used for vaporizations, but the atom flux and secondary electron flux are coincident, and the latter is the source of significant independent chemistry.[4] A 30-mil tungsten or molybdenum wire is easily heated with currents of 30–50 A (11–20 V) to temperatures suitable for vaporizations into the 10^{-5} Torr vacuum, at rates of 1–2 mmol/hr.

Cocondenᵃation at −196° of the metal atoms with the chosen arenes (molar ratios 100) results in formation of brightly colored matrices. On warming to room temperature the solutions of products in excess arene are siphoned out of the reaction system and isolated by sublimation (after removing excess substrate) at temperatures of 50–80° at pressures less than 10^{-3} Torr. From runs in which 200–250 mg of metal is vaporized, the pure products are isolated in yields of 30–50%. Some of the products are shown in Table I. With the exception of the red molybdenum methylbenzoate and dimethylaniline products, the others are green or yellow-green.

The mass spectra (with expected isotope patterns) and proton magnetic resonance spectra serve to identify these products. Electron impact ionization to P⁺ is a dominant process; fragmentation to molybdenum-

containing ions occurs by loss of one or both arenes; no tungsten-containing fragments were observed.

The unique synthetic value of this method is illustrated by the preparation involving O, N, and halogen containing substituents.

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Flash Cadmium Photosensitization Studies. II. Absolute Rate Constants for the Quenching of Cadmium($5^3P_{0,1}$) Atoms

Sir:

The quenching reactions of Cd(5^3P) atoms have been extensively investigated and absolute rate constants determined for a variety of quenchers using conventional fluorescence techniques.[1,2]

In a recent communication from this laboratory[3] we described a novel flash photolysis–kinetic absorption spectroscopic technique for the study of the room temperature quenching reactions of triplet cadmium atoms. It was shown that equilibration of the $^3P_1$ and $^3P_0$ states is facile and in fact it is not possible to study the reactions of either state separately. The measured value of the decay rate constant of Cd($^3P_{0,1}$) atoms in the presence of ethylene was some two orders of magnitude smaller than the earlier value of the Cd($^3P_1$) quenching rate constant and it was concluded that conventional fluorescence techniques are not applicable for the determination of absolute rate constants for the quenching of Cd(5^3P_1) atoms. The discrepancy can be attributed primarily to the intervention of $^3P_0$ atoms in the reaction and to some extent to the effect of imprisonment on the fluorescence lifetime in the conventional measurements. Also, the technique used for calibration of the photographic plates in the early conventional studies was not fully satisfactory.

(2) F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J. Chem. Soc., Chem. Commun.*, 866 (1973).
(3) (a) P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Accounts Chem. Res.*, 6, 97 (1973); (b) P. S. Skell, L. D. Westcott, Jr., J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 2829 (1965).
(4) P. S. Skell and P. W. Owen, *J. Amer. Chem. Soc.*, 94, 5434 (1972).

(1) H. C. Lipson and C. G. Mitchell, *Phys. Rev.*, 48, 625 (1935).
(2) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, 11, 164 (1943).
(3) P. J. Young, G. Greig, and O. P. Strausz, *J. Amer. Chem. Soc.*, 92, 413 (1970).