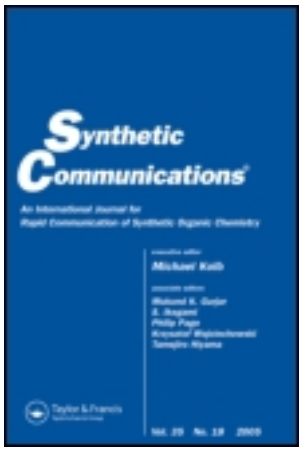


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Intramolecular Biaryl Oxidative Coupling of Stilbenes by Vanadium Oxytrichloride ($VOCl_3$): Facile Synthesis of Substituted Phenanthrene Derivatives

Zhong Jin [a], Qingmin Wang [a] & Runqiu Huang [a]

[a] Institute and State Key Laboratory of Elemento-organic Chemistry, Nankai University, Weijin Road 94#, Tianjin, 300071, P.R. China

Version of record first published: 16 Aug 2006.

To cite this article: Zhong Jin , Qingmin Wang & Runqiu Huang (2004): Intramolecular Biaryl Oxidative Coupling of Stilbenes by Vanadium Oxytrichloride ($VOCl_3$): Facile Synthesis of Substituted Phenanthrene Derivatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:1, 119-128

To link to this article: http://dx.doi.org/10.1081/SCC-120027245

SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 1, pp. 119–128, 2004

Intramolecular Biaryl Oxidative Coupling of Stilbenes by Vanadium Oxytrichloride ($VOCl_3$): Facile Synthesis of Substituted Phenanthrene Derivatives

Zhong Jin, Qingmin Wang, and Runqiu Huang*

Institute and State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin, P.R. China

ABSTRACT

Vanadium oxytrichloride ($VOCl_3$) has proven to be a highly efficient reagent for intramolecular biaryl oxidative coupling reaction of electron-rich stilbenes. Accordingly, a mild and efficient route to phenanthrene derivatives from stilbenes oxygenated is developed.

Key Words: Vanadium oxytrichloride; Biaryl oxidative coupling; Stilbenes; Phenanthrene derivatives.

*Correspondence: Runqiu Huang, Institute and State Key Laboratory of Elemento-organic Chemistry, Nankai University, Weijin Road 94#, Tianjin 300071, P.R. China; Fax: +86 022 2350 3438; E-mail: jinzhong2000@263.net.

DOI: 10.1081/SCC-120027245
0039-7911 (Print); 1532-2432 (Online)

www.dekker.com

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

The biaryl unit is extensively presented in many classes of natural products, such as polyketides, terpenes, lignanes, coumarins, flavonoids, tannins, and many alkaloids.[1] It has long been recognized that an intramolecular oxidative phenolic or nonphenolic coupling reaction serves as the key step in the biosynthesis of these natural products, and the non-enzymic analogue of this transformation can lead the elegantly simple syntheses of these compounds.[2] During the last decade, a large number of oxidative coupling reagents, such as ferric chloride ($FeCl_3$),[3–5] phenyliodine(III) bis(trifluoroacetate) (PIFA),[6–8] lead(IV) tetraacetate ($Pb(OAc)_4$),[9] thallium(III) triflouroacetate (TTFA),[10,11] as well as vanadium oxytrifluoride (VOF_3),[12–15] have been developed for this target. However, extensive application of this synthetic potential has been limited by low yields and unexpected side reactions usually encountered.

As part of the total syntheses of Asclepiadaceae alkaloids, several polymethoxyphenanthrene derivatives were required, but they were found to be tediously accessible by conventional Ullman's method. After comprehensive investigation, vanadium oxytrichloride ($VOCl_3$) is found to be very efficient reagent for this type of oxidative coupling reaction due to its liquid property and solubility in most reaction media. Herein, we report a concise and efficient pathway for substituted phenanthrene by intramolecular biaryl oxidative coupling utilizing $VOCl_3$ as an oxidant.

Condensation of substituted phenylacetic acids **1** and aromatic aldehydes **2** was carried out in refluxing acetic anhydride in the presence of triethylamine with excellent yields.[16] Although the product thus obtained is invariably a mixture of *Z*- and *E*-α-(arylmethylene)phenylacetic acids **3**, both of them can be used for subsequent intramolecular oxidative coupling. On treatment with ethereal diazomethane, acids **3** were smoothly transformed into corresponding methyl esters **4** in almost quantitative yields. Oxidation of **4** with $VOCl_3$ in dichloromethane at $-78^{\circ}C$ afforded the methyl phenanthrene-9-carboxylates **5** in moderate to excellent yields (Table 1, entry 1–5). The coupling occuring from C6 and C6′ of **4a** to give **5a** is evident from the appearance of four single peaks in the phenanthrene ring in the ^1H NMR spectrum of compound **5a**. In addition, it is noteworthy that both (*Z*)- and (*E*)-**4** gave the same products under this condition (Sch. 1).

The above result shows that two methoxy groups are necessary in at least one of the aromatic rings. However, the fact that esters **4**, which bear m-dimethoxy substituents, do not cyclize implies that the two groups should be ortho-disposed. Furthermore, 2,3-dimethoxy derivative **4** fail to deliver corresponding **5**, what implies that aromatic rings of substrates with oxygen functionality at the 3- and 4- and/or 3′- and 4′-positions are essential to afford oxidative cyclization.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table 1. Intramolecular oxidative coupling of stilbene substrates with $VOCl_3$.

	Stilbene substrate[a]							
Entry	No.	R_1	R_2	R_3	R_4	R	Product	Yield[b]
1	**4a**	OCH_3	OCH_3	OCH_3	OCH_3	CO_2CH_3	**5a**	98
2	**4b**	OCH_3	OCH_3	OCH_3	H	CO_2CH_3	**5b**	82
3	**4c**	OCH_3	OCH_3	H	H	CO_2CH_3	**5c**	76
4	**4d**	OCH_3	H	OCH_3	OCH_3	CO_2CH_3	**5d**	72
5	**4e**	H	H	OCH_3	OCH_3	CO_2CH_3	**5e**	54
6	**4f**	OCH_3	OCH_3	OCH_3	OCH_3	CN	**5f**	97
7	**4g**	OCH_3	OCH_3	H	H	CN	**5g**	58
8	**4h**	OCH_3	OCH_3	OCH_3	OCH_3	NO_2	**5h**	96
9	**4i**	OCH_3	OCH_3	H	H	NO_2	**5i**	61

[a]A mixture of *Z*- and *E*-isomer in entry 1–5, only *Z*-isomer in entry 6–9.
[b]Isolated yields.

Similarly, when ester group of **4** on the double bond was replaced by a nitro or cyano group (Sch. 2), the (α-nitro/cyano)stilbenes **4f–i** prepared from (3,4-dimethoxy)nitromethylbenzene[17] **6** or (3,4-dimethoxyphenyl)acetonitriles 7 with aromatic aldehydes **2** were readily for oxidative cyclization to the corresponding phenananthrene derivatives **5** in moderate to excellent yields (Table 1, entry 6–9).

In order to examine the generality of phenanthrene derivatives formation by this means, effects of substituents on the double bond of stilbene substrates were studied in detail. When ester group on the double bond was replaced by an electron-donating group such as a hydroxyl or methoxyl group, no coupling product **8** was formed. Further investigation shows that stilbene also fail to give phenanthrene derivative **9**. However, compounds **8** and **9** may be easily obtained from corresponding nitro compound **5h**. Reduction of **5h** with ferrous sulfate afforded corresponding 2,3,6,7-tetramethoxy-9-aminophenanthrene **10** in a yield of 86%, further treatment with sodium nitrite in hydrochloric acid to yield corresponding diazo compound, which was subsequently transformed to the desired phenanthrene derivatives **8** and **9** in a yield of 66% and 74%, respectively (Sch. 3).

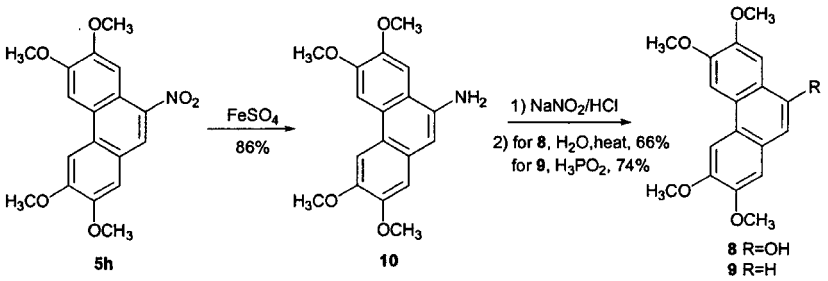
From above results we believed that, in addition to substitution effect on two aryl groups, intramolecular biaryl coupling of stilbene substrates was also sensitive to substituents on the double bond. Particularly, this reaction fails in absence of electron-donating substituents. Up now, to the best of our knowledge, no mechanism has yet been formulated for coupling reactions employing the vanadium reagents, but it is believed to involve electron

Scheme 1.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Scheme 2.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016



Scheme 3.

transfer and form radical cations on electron rich substrates.[18,19] If this is the case, it therefore seems likely that electron-donating group increases the electron-density on the double bond of stilbene substrates. As a result, double bond is oxidized prior to aromatic rings. Whereas, with an electron-withdrawing group on double bond, aryl rings of substrates will be oxidized prior to double bond and form aromatic radical cations.

In summary, a mild and efficient route to phenanthene derivatives from stilbenes oxygenated by intramolecular biaryl oxidative coupling with $VOCl_3$ has been described. Effect of substitution on stilbene substrates has been examined and an electron-withdrawing group on the double bond has proven to be essential for the oxidative coupling. Application this oxidative coupling method for the total synthesis of Asclepiadaceae and Amaryllidaceous alkaloids is under investigation.

EXPERIMENTAL

All solvents were distilled from sodium/benzophenone prior to use. All melting points were uncorrected. ^{1}H NMR were recorded on a BRUKER AC-P 200 using tetramethylsilane as the internal standard. Elemental analyses were performed on a Yanaco CHN CORDER MT-3 instrument.

Representative Procedure for Intramolecular Oxidative Coupling

A solution of 10.8 g (30 mmol) of methyl (*Z*,*E*)-α-(arylmethylene)phenylacetate **4** in 500 mL of dichloromethane was cooled to -78°C with well stirred under N_2. Then, 5.7 mL (33 mmol) of $VOCl_3$ was added in one portion at this point. After being stirred for 16 hours at -50°C, the reaction mixture was quenched with cold water, and the organic phase was well washed with

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

saturated brine (3 × 150 mL). Then the organic phase was dried over $MgSO_4$, filtered through a short silica gel column, and evaporated to give desired products, methyl phenanthrene-9-carboxylate **5** in 55–98% yields. The following compounds were obtained:

Methyl 2,3,6,7-tetramethoxyphenanthrene-9-carboxylate (5a). 98% yield, white solid, m.p. 202–204°C (lit.[20] 202–204°C). 1H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.64 (s, 1H), 8.41 (s, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 7.25 (s, 1H), 4.14 (s, 3H), 4.13 (s, 3H), 4.08 (s, 3H), 4.04 (s, 3H), 4.02 (s, 3H). EI-MS m/z: 356 (M^+, 100). Anal. calcd. for $C_{20}H_{20}O_6$: C, 67.41, H, 5.66; Found: C, 67.45, H, 5.71.

Methyl 3,6,7-trimethoxyphenanthrene-9-carboxylate (5b). 82% yield, white solid, m.p. 155–156°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H), 8.20 (s, 1H), 8.10 (s, 1H), 7.75 (s, 1H), 7.44 (m, 2H), 4.15 (s, 3H), 4.06 (s, 3H), 4.05 (s, 3H), 3.97 (s, 3H). Anal. calcd. for $C_{19}H_{18}O_5$: C, 69.93, H, 5.56; Found: C, 69.73, H, 5.60.

Methyl 6,7-dimethoxyphenanthrene-9-carboxylate (5c). 76% yield, white solid, m.p. 130–131°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.40 (s, 1H), 8.28 (s, 1H), 8.18 (s, 1H), 7.8–7.4 (m, 4H), 4.00 (s, 3H), 3.96 (s, 3H), 3.92 (s, 3H). Anal. calcd. for $C_{18}H_{16}O_4$: C, 72.96, H, 5.44; Found: C, 72.78, H, 5.62.

Methyl 2,3,7-trimethoxyphenanthrene-9-carboxylate (5d). 72% yield, white solid, m.p. 148–149°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.48 (s, 1H), 8.26 (s, 1H), 8.15 (s, 1H), 7.8–7.6 (m, 2H), 7.50 (s, 1H), 4.10 (s, 3H), 3.99 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H). Anal. calcd. for $C_{19}H_{18}O_5$: C, 69.93, H, 5.56; Found: C, 69.92, H, 5.83.

Methyl 2,3-dimethoxyphenanthrene-9-carboxylate (5e). 54% yield, white solid, m.p. 142–144°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.78 (s, 1H), 8.24 (s, 1H), 8.05 (s, 1H), 7.6–7.4 (m, 3H), 6.99 (s, 1H), 4.10 (s, 3H), 3.99 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H). Anal. calcd. for $C_{18}H_{16}O_4$: C, 72.96, H, 5.44; Found: C, 72.92, H, 5.26.

9-Cyano-2,3,6,7-tetramethoxyphenanthrene (5f). 97% yield, white solid, m.p. 133–134°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.98 (s, 1H), 8.45 (s, 1H), 8.25 (s, 1H), 7.6 (s, 1H), 7.4 (s, 1H), 4.15 (s, 3H), 4.09 (s, 3H), 4.07 (s, 3H), 4.02 (s, 3H). Anal. calcd. for $C_{18}H_{17}NO_6$: C, 62.97, H, 4.99, N, 4.08; Found: C, 62.89, H, 5.07, N, 4.10.

9-Cyano-6,7-dimethoxyphenanthrene (5g). 58% yield, light yellow solid, m.p. 125–127°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.83 (s, 1H), 8.39 (s, 1H), 8.00 (s, 1H), 7.9–7.6 (m, 4H), 4.11 (s, 3H), 4.02 (s, 3H). Anal. calcd. for $C_{16}H_{13}NO_4$: C, 67.84, H, 4.63, N, 4.94; Found: C, 67.91, H, 4.66, N, 4.80.

9-Nitro-2,3,6,7-tetramethoxyphenanthrene (5h). 96% yield, yellow solid, m.p. 156–157°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.71 (s, 1H),

8.34 (s, 1H), 8.18 (s, 1H), 7.60 (s, 1H), 7.49 (s, 1H), 4.10 (s, 3H), 4.00 (s, 3H), 3.99 (s, 3H), 3.95 (s, 3H). Anal. calcd. for $C_{19}H_{17}NO_4$: C, 70.58, H, 5.30, N, 4.33; Found: C, 70.52, H, 5.66, N, 4.50.

9-Nitro-6,7-dimethoxyphenanthrene (5i). 61% yield, yellow solid, m.p. 139–142°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.78 (s, 1H), 8.39 (s, 1H), 7.99 (s, 1H), 7.7–7.5 (m, 4H), 4.05 (s, 3H), 3.95 (s, 3H). Anal. calcd. for $C_{17}H_{13}NO_2$: C, 77.55, H, 4.98, N, 5.32; Found: C, 77.72, H, 5.01, N, 5.40.

9-Amino-2,3,6,7-tetramethoxyphenanthrene (10). To a solution of the 9-nitro-2,3,6,7-tetramethoxyphenanthrene **5h** (3.43 g, 10 mmol) in 95% aqueous EtOH (100 mL) was added ferrous sulfate heptahydrate (20 g) dissolved in distilled water (100 mL) and concentrated aqueous NH_4OH (100 mL). The reaction mixture was refluxed for 2 h, cooled to room temperature, filtered on Celite and acidified with acetic acid. The solid was collected by filtration and recrystallization from EtOH yielded the 9-amino-phenanthrene **10** in 86% yield, brown solid, m.p. 225–226°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 1H), 7.74 (s, 1H), 7.08 (s, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 4.11 (s, 3H), 4.09 (s, 3H), 4.07 (s, 3H), 4.04 (s, 3H), 2.90–2.60 (br, 2H). Anal. calcd. for $C_{18}H_{19}NO_4$: C, 68.99, H, 6.11, N, 4.47; Found: C, 68.85, H, 6.18, N, 4.66.

9-Hydroxy-2,3,6,7-tetramethoxyphenanthrene (8). To a cooled solution of concentrated H_2SO_4 (10 mL) in distilled water (60 mL) was added 9-amino-phenanthrene **10** (3.13 g, 10 mmol). The mixture was cooled to 0°C in an ice bath with stirring. To the reaction mixture was added a solution of sodium nitrite (2.1 g, 30 mmol) in water (15 mL). After stirred at the room temperature for 2 h, 50 mL distilled water was added. The mixture was refluxed for 1 h, cooled, filtered. The filtrate was extracted with $CHCl_3$ (3 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated to yield the corresponding 9-hydroxy-phenanthrene **8** in 66% yield, pale solid, m.p. 267–268°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.98 (br s, 1H), 8.69 (s, 1H), 7.88 (s, 1H), 7.7 (s, 1H), 7.68 (s, 1H), 6.95 (s, 1H), 4.05 (s, 3H), 3.95 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H). Anal. calcd. for $C_{18}H_{18}O_5$: C, 68.78, H, 5.77; Found: C, 68.72, H, 5.71.

2,3,6,7-Tetramethoxyphenanthrene (9). To a cooled solution of concentrated HCl (10 mL) in distilled water (15 mL) was added 9-amino-phenanthrene **10** (3.13 g, 10 mmol). The mixture was cooled to 0°C in an ice bath with stirring. To the reaction mixture was added a solution of sodium nitrous (2.1 g, 30 mmol) in water (15 mL) at 0°C. After stirred at 0°C for 2 h, the mixture was filtered. The filtrate was added into aqueous H_3PO_2 (50%, 80 mL). The mixture was stirred at 0° for 2 h and extracted with $CHCl_3$ (3 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated to yield the corresponding 2,3,6,7-tetramethoxyphenanthrene **9** in 74% yield, m.p. 181°C, (lit.[21] m.p. 180–181°C). ^{1}H NMR (200 MHz,

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

$CDCl_3$) δ (ppm): 7.77 (s, 2H), 7.54 (s, 2H), 4.10 (s, 6H), 4.02 (s, 6H). Anal. calcd. for $C_{18}H_{18}O_4$: C, 72.47, H, 6.08; Found: C, 72.74, H, 5.99.

ACKNOWLEDGMENT

We gratefully acknowledge the National Natural Science Foundation of China (NNSFC) (No. 20002003) for financial support.

REFERENCES

1. Bringmann, G.; Walter, R.; Weirich, R. The direct synthesis of biaryl compounds: modern concepts and strategies. Angew. Chem. Int. Ed. Engl. **1990**, *29*, 977.
2. Dhingra, O.P. *Oxidation in Organic Chemistry, Part D*; Trahanovsky, W.S., Ed.; Academic Press: New York, 1982; 207.
3. Herbert, R.B.; Kattah, A.E.; Murtagh, A.J.; Sheldrake, P.W. Use of iron (III) chloride in the efficient preparation of the alkaloid kreysigine by oxidative coupling. Tetrahedron Lett. **1995**, *36*, 5649.
4. Tanaka, M.; Mukaiyama, C.; Mitsuhashi, H.; Maruno, M.; Wakamatsu, T. Synthesis of optically pure gomisi ligans: the total synthesis of (+)-schizandrin, (+)-gomision A, and (+)-isoschizandrin in naturally occurring forms. J. Org. Chem. **1995**, *60*, 4339.
5. Murase, M.; Kotani, E.; Okazaki, K.; Tobinaga, S. Application of iron (III) complexes. *Tris*(2,2′-bipyridyl)iron (III) perchlorate and some iron(III) solvates, for oxidative aryl–aryl coupling reactions. Chem. Pharm. Bull. **1986**, *34*, 3159.
6. Tohma, H.; Morioka, H.; Takizawa, S.; Arisawa, M.; Kita, Y. Efficient oxidative biaryl coupling reaction of phenol ether derivatives using hypervalent iodine (III) reagents. Tetrahedron **2001**, *57*, 345.
7. Takada, T.; Arisawa, M.; Gyoten, M.; Hamada, R.; Tohma, H.; Kita, Y. Oxidative biaryl coupling reaction of phenol ether derivatives using a hypervalent iodine (III) reagent. J. Org. Chem. **1998**, *63*, 7698.
8. Kita, Y.; Gyoten, M.; Ohtsubo, M.; Tohma, H.; Takada, T. Non-phenolic oxidative coupling of phenol ether derivatives using phenyl iodine (III) bis(trifluoroacetate). Chem. Commun. **1996**, 1481.
9. Feldman, K.S.; Ensel, S.M. Ellegitannin chemistry. Preparative and mechanistic studies of the biomimetic oxidative coupling of galloyl esters. J. Am. Chem. Soc. **1994**, *116*, 3357.
10. Buckleton, J.S.; Cambie, R.C.; Clark, G.R.; Craw, P.A.; Rickard, C.E.F.; Rutledge, P.S.; Woodgate, P.D. Oxidative coupling of ligans. II. Non-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

phenolic coupling of diarylbutane ligans related to matairesinol dimethyl ether. Aust. J. Chem. **1988**, *41*, 305.
11. Taylor, E.C.; Andrade, J.G.; Rall, G.J.H.; McKillop, A. Thallium in organic synthesis. 59. Alkaloid synthesis via intramolecular nonphenolic oxidative coupling. Preparation of (±)-ocoteine, (±)-acetoxyocoxylonine, (±)-3-methoxy-N-acetylnornantenine, (±)-neolitsine, (±)-kreysigine, (±)-*O*-methylkreysigine, and (±)-multifloramine. J. Am. Chem. Soc. **1980**, *102*, 6513.
12. Lienard, P.; Saint-Jalmes, B.; Quirion, J. Aza-dibenzocyclooctadiene analogue of stegane via the CN (R, S) method. Tetrahedron Lett. **1995**, *36*, 5895.
13. Evans, D.A.; Dinsmore, C.J.; Evrard, D.A.; DcVries, K.M. Oxidative coupling of arylglycine-containing peptides. A biomimetic approach to the synthesis of the macrocyclic actinoidnic-containing vancomycin subunit. J. Am. Chem. Soc. **1993**, *115*, 6426.
14. Comins, D.L.; Morgan, L.A. N-acylcihydropyridones as synthetic intermediates. Synthesis of (±)-septicine and (±)-tylophorine. Tetrahedron Lett. **1991**, *32*, 5919.
15. Halton, B.; Maidment, A.I.; Officer, D.L.; Warner, J.M. The oxidative conversion of (*E*)-α-(arylmethylene)-benzeneacetate into substituted phenanthrenes: the propitious use of boron trifluoride with vanadium trifluoride oxide. Aust. J. Chem. **1984**, *37*, 2119.
16. Russel, J.H.; Hunziker, H. Synthesis of septicine. Tetrahedron Lett. **1969**, 4035.
17. Stiefel, F.J.. Synthesis of 2-phenyl-1,3-propanediol. US 5,072,056, 1991.
18. Hirao, T. Vanadium in modern organic synthesis. Chem. Rev. **1997**, *97*, 2707.
19. Sainsbury, M. Modern methods of aryl–aryl bond formation. Tetrahedron **1980**, *36*, 3327 and references cited therein.
20. Cragg, E.E.; Herbert, R.B.; Jackson, F.B.; Moody, C.J.; Nicolson, I.T. Phenanthroindolizidine and related alkaloids: synthesis of tylophorine, septicine, and deoxytylophorine. J. Chem. Soc. Perkin Trans. 1. **1982**, 2477.
21. Nordlander, J.E.; Njoroge, F.G. A short synthesis of *S*-(+)-tylophorine. J. Org. Chem. **1987**, *52*, 1627.

Received in Poland April 8, 2003

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016