hydrofuran freshly distilled until no **2Z** was noticed by thin-layer chromatography. The solution was concentrated in vacuo and the resultant yellow oil dried. The whole yellow solid was dissolved in the minimum amount of warm benzene, and the three compounds of the mixture were separated by column chromatography (SiO_2, 70–230 mesh) using benzene as eluting agent to afford analitically pure samples of the three compounds in this order: first 450 mg (42%) of (*Z*)-2-methyl-4-(α-phenylethylidene)-5-(4*H*)-oxazolone (**6Z**), mp 116–117 °C, IR (Nujol) 1770 (C=O) [Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.47; N, 6.97. Found: C, 71.73; H, 5.36; N, 6.95,]; later 95 mg (9%) of (*Z*)-1-phenyl-5-methyl-6-oxa-4-azaspiro[2.4]hept-4-en-7-one (**4Z**), mp 193–194 °C, IR (Nujol) 1810 (C=O) [Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.47; N, 6.97. Found: C, 71.89; H, 5.62; N, 6.93,]; and finally 43 mg (4%) of (*E*)-1-phenyl-5-methyl-6-oxa-4-azaspiro[2.4]-hept-4-en-7-one (**4E**), mp 218–219 °C; IR (Nujol) 1800 (C=O) [Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.47; N, 6.97. Found: C, 71.50; H, 5.38; N,7.09.].

Registry No. **1E**, 15732-43-1; **1Z**, 17606-70-1; **2Z**, 38879-46-8; **3E**, 64283-24-5; **3Z**, 64283-23-4; **4E**, 87378-64-1; **4Z**, 87378-66-3; **5E**, 57427-91-5; **5Z**, 69015-75-4; **6Z**, 87378-63-0; benzaldehyde, 100-52-7; aceturic acid, 543-24-8; hippuric acid, 495-69-2; diazomethane, 334-88-3.

Studies Aimed at the Synthesis of Morphine. 7.[1] Biomimetic Total Synthesis of (±)-Pallidine

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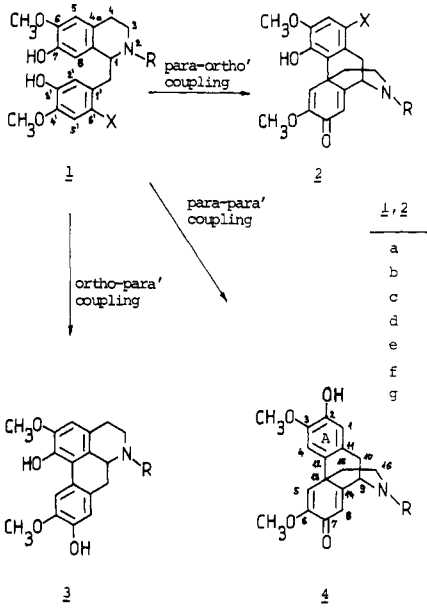
Received October 4, 1983

In plants morphinandienone-type alkaloids arise via phenolic oxidative coupling of 1-benzyl-1,2,3,4-tetrahydroisoquinolines. This transformation, which is considered to be the key step of the biogenesis of morphinans as well, has been suggested by Gulland and Robinson[2] and confirmed and refined by Barton and Cohen.[3] The first step of the reticuline (**1a**) → salutaridine (**2a**) → thebaine → morphine pathway requires a regioselective para–ortho′ oxidative coupling, which was in vitro detected (0.03% yield determined by an isotope dilution technique) first by Barton et al.[4] in 1963 and realized recently in preparative scale (2.7%) by our group[5] using lead tetraacetate in the presence of trichloroacetic acid. The great many attempts for the oxidation of reticuline (**1a**) using MnO_2,[6] $K_3Fe(CN)_6$,[4b,7] $AgCO_3$/Celite,[7d] and $VOCl_3$[7d,8] afforded mainly aporphinic isoboldine (**3a**) (ortho–para′ coupling) and isosalutaridine (**4a**) (para–para′) in 0.3–4% yield[9] (Scheme I). The dextrorotatory antipode of the latter has also been found as an alkaloid of *Corydalis pallida* var. *tenuis* (Yatabe) named pallidine.[13]

Scheme I



1,2	R	X
a	CH_3	H
b	$CO_2C_2H_5$	H
c	$CO_2C_2H_5$	Br
d	$CO_2C_2H_5$	Cl
e	CHO	H
f	CHO	Br
g	CHO	Cl

3,4	R
a	CH_3
b	$CO_2C_2H_5$
c	CHO

In the biomimetic approach of morphine the para–ortho′ coupling has been accomplished in remarkably higher yield, when instead of reticuline (**1a**), *N*-acylnorreticulines **1b–g** were used as starting materials. In these oxidative cyclizations thallium tris(trifluoroacetate),[14,15] lead tetraacetate, or different organic iodo compounds[1,16] proved to be effective in supplying *N*-acylnorsalutaridines **2b–g** regioselectively.

Now we report the successful utilization of manganese and vanadyl acetonylacetonate for the selective formation of *N*-acylnorisosalutaridines **4b,c** via para–para′ coupling of the corresponding *N*-acylnorreticulines.

Treatment of *N*-(ethoxycarbonyl)norreticuline (**1b**)[16,17,21] with 5 equiv of manganese tris(acetonylacetonate) in boiling absolute acetonitrile afforded *N*-(ethoxycarbonyl)norisosalutaridine (**4b**) in 32% yield[18] along with a small amount of *N*-(ethoxycarbonyl)norisoboldine (**3b**).

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(18) All of our yields are corrected with the recovered starting material.

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Similar results could be achieved (27% of **4c**) by starting with *N*-formylnorreticuline (**1e**);[16,19,21] however, in this case a larger amount of starting material remained unreacted.

The IR and UV spectra of the compounds **4b,c** verifies the formation of a morphinandienone structure, and the four singlets for aromatic and vinyl protons in the ^{1}H NMR spectrum unambiguously prove the isosalutaridine-type substitution pattern of ring A (see Experimental Section). It is worth mentioning that some of the ^{1}H and ^{13}C NMR signals of **4c** appeared as doubled peaks due to the hindered rotation of the *N*-formyl group.[20,21]

According to our earlier experiences, halogen substituent at C-6′ protected the para′ position when lead tetraacetate or different organic iodo compounds were used as oxidants, and a higher regioselectivity in formation of *N*-acylnorsalutaridines was observed.[1,16] To investigate this protecting effect and the possibility of obtaining salutaridine-type compounds with manganese tris(acetonylacetonate), similar oxidation of 6′-bromo-*N*-(ethoxycarbonyl)- (**1c**) and 6′-bromo-*N*-formylnorreticuline[16,21] (**1f**) were performed. Interestingly enough under the conditions applied the new linkage arises mostly between carbon atoms 4a and 6′ of **1c** and **1f** to supply *N*-acylnorisosalutaridine derivatives **4b** and **4c**, respectively; during the process, consequently, elimination of the bromine takes place. From the coupling reaction of **1c** or **1f** using manganese tris(acetonylacetonate), 33% **4b** or 29% **4c** and 6% **2c** or about 3% **2f**, respectively, could be isolated and the formation of the corresponding *N*-acylnorisoboldines **3b** or **3c** was detected only in traces by TLC.

Similar results have been experienced with vanadyl bis(acetonylacetonate) as oxidant.

(±)-Pallidine (**4a**) could be obtained from *N*-formylnorisosalutaridine (**4c**) via deformylation and subsequently the Eschweiler–Clark methylation process. The spectroscopic data of racemic **4a** correspond to those of natural pallidine reported in the literature.[13]

Experimental Section

Melting points are uncorrected. UV spectra were taken in methanol on a Unicam SP-700 spectrophotometer. IR spectra were recorded on Nicolet-7199 and Spectromom 2000 infrared spectrophotometers. ^{1}H NMR spectra were determined on a Varian XL-100-15 instrument using deuteriochloroform as solvent and Me_3Si as internal standard. Chemical shifts are reported as δ values. ^{13}C NMR spectra were determined on the same spectrometer operating in the FT mode at 25.16 MHz. Mass spectra were obtained with an AEI MS-902 instrument (70 eV, direct insertion). Silica gel PF_{254} coated plates (E. Merck) were used for the purposes of qualitative TLC and preparative-layer chromatography.

General Procedure for the Oxidative Cyclization. *N*-Acylnorreticuline (0.8 mmol) was dissolved in absolute acetonitrile (200 mL), and manganese tris(acetonylacetonate) (1.42 g, 4 mmol) was added. The reaction mixture was refluxed for 5 h in an argon atmosphere. The reaction was monitored by TLC on plates pretreated in NH_3 vapor for 5 min, using a dichloromethane–methanol (10:1, v/v) system. The reaction mixture was evaporated under reduced pressure. The residue was taken up in chloroform (250 mL), and extracted with 5% NH_4OH solution and water consecutively, the last two extracts were reextracted with a small amount of chloroform. The combined organic phase was dried over $MgSO_4$ and evaporated in vacuo. The residue was separated by repeated preparative TLC using first a dichloromethane–methanol (100:5, v/v) solvent system and for final purification DC Fertigplatten Kieselgel 60 plates (Merck) and a dichloromethane–methanol (100:10, v/v) system in NH_3 vapor.

Table I. ^{13}C NMR Spectral Data of 4b and 4c in $CDCl_3$[a]

carbon assignment	chemical shifts, ppm 4b	4c
1	114.2	114.0 + 114.2
2	145.3+	145.5 + 145.6*
3	146.3+	146.5 + 146.6*
4	108.0	108.1
5	118.7*	118.2 + 118.3
6	159.6	158.1
7	180.8	180.4 + 180.5
8	121.9*	121.7 + 122.4
9	52.7	49.3 + 55.8
10	37.9	38.1 + 39.4
11	128.0	127.3 + 127.9
12	128.6	128.3 + 128.5
13	42.5	43.3 + 43.4
14	151.6	151.6 + 151.7
15	41.8	41.4 + 42.2
16	38.4	34.4 + 40.3
17	155.4	160.8 + 161.0
3-OCH_3	56.3	56.3
6-OCH_3	55.2	55.2
CH_3CH_2O	61.9	
CH_3CH_2O	14.7	

[a] The values marked with identical symbols are interchangeable.

Preparation of *N*-(Ethoxycarbonyl)norisosalutaridine (4b). Starting with **1b** (310 mg, 0.8 mmol), 65.2 mg of **4b** (32%) and 8.2 mg of **3b** (4%) were obtained and 105 mg of **1b** was recovered.

4b: mp 146–150 °C (ether-hexane); UV (MeOH) λ_{max} 240 nm (log ϵ 4.34), 287 (3.92); IR ($CHCl_3$) ν_{max} 3320 cm^{-1} (OH), 1695 (NC=O), 1670, 1650, 1625 (cyclohexadienone); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1, 28 (t, J = 7 Hz, 3 H, CH_2CH_3), 3.78 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 4.18 (q, J = 7 Hz, 2 H, CH_2CH_3), 5.18 (m, 1 H, H-9), 6.34 (s, 1 H, H-8), 6.38 (s, 1 H, H-1), 6.68 (s, 1 H, H-4), 6.85 (s, 1 H, H-5); ^{13}C NMR see Table I; mass spectrum, *m/e* (relative intensity) 385 (M^+, 100), 384 (5), 370 (5), 367 (16), 357 (12), 356 (16), 353 (9), 340 (7), 339 (9), 326 (6), 325 (5), 324 (3), 312 (23), 310 (11), 296 (29), 284 (30), 283 (76), 270 (30), 269 (18), 255 (10), 241 (8), 227 (9).

3b: amorphous; UV (MeOH) λ_{max} 280 nm (log ϵ 3.81), 303 (3.88); IR (KBr) ν_{max} 3400 cm^{-1} (OH), 1690 (C=O); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.23 (t, J = 7 Hz, 3 H, CH_2CH_3), 3.91 (s, 6 H, 2 × OCH_3), 4.20 (q, J = 7 Hz, 2 H, CH_2CH_3), 4.75 (m, 1 H, H-6a), 6.56 (s, 1 H, H-3), 6.82 (s, 1 H, H-8), 8.14 (s, 1 H, H-11); mass spectrum, *m/e* (relative intensity) 385 (M^+, 100), 357 (12), 356 (15), 312 (13), 310 (19), 284 (34), 283 (78), 250 (23).[22]

Starting with **1c** (370 mg, 0.8 mmol), 58.8 mg of **4b** (33%), 12.7 mg of **2c** (6%), and 154 mg of unreacted **1c** were separated. Compound **2c** was identical in every respect with that obtained earlier by us, see ref 16.

If vanadyl bis(acetonylacetonate) was used as oxidant from **1c** (185 mg, 0.4 mmol), 23.2 mg of **4b** (24%) and 68 mg of unreacted **1c** could be obtained.

Preparation of *N*-Formylnorisosalutaridine (4c). Starting with **1e** (275 mg, 0.8 mmol), 36.2 mg of **4c** (27%) and 4 mg of **3c** (3%) were obtained and 135 mg of **1e** was recovered.

4c: amorphous; UV (MeOH) λ_{max} 240 nm (log ϵ 4.25), 288 (3.86); IR ($CHCl_3$) ν_{max} 3300 cm^{-1} (OH), 1670 (>C=O and NC=O), 1650, 1625 (cyclohexadiene); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 3.78 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3); 4.56 and 5.48 (m, m, 1 H, H-9), 6.36 (s, 1 H, H-8), 6.40 (s, 1 H, H-1), 6.70 (s, 1 H, H-4), 6.85 (s, 1 H, H-5), 8.05 and 8.20 (s, s, 1 H, NCHO); ^{13}C NMR see Table I; mass spectrum, *m/e* (relative intensity) 341 (M^+, 100), 340 (13), 326 (10), 324 (31), 323 (20), 313 (21), 309 (16), 296 (50), 284 (30), 283 (98), 281 (23), 270 (42), 269 (65), 268 (15), 255 (19), 253 (15), 241 (17), 240 (14), 227 (17).

3c: amorphous; UV (MeOH) λ_{max} 280 nm (log ϵ 3.85), 302 (3.95); IR (KBr) ν_{max} 3400 cm^{-1} (OH), 1660 (C=O); ^{1}H NMR ($CDCl_3$ +

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(22) The spectral data we obtained compare well with the literature data in ref 17.

Me_2SO-d_6, 100 MHz) δ 3.88 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.77 and 4.92 (m, m, 1 H, H-6a), 6.52 and 6.57 (s, s, 1 H, H-3), 6.77 and 6.81 (s, s, 1 H, H-8), 8.06 and 8.15 (s, s, 1 H, H-11), 8.24 and 8.34 (s, s, 1 H, NCHO); mass spectrum, *m/e* (relative intensity) 341 (M^+, 96), 326 (4), 324 (5), 313 (9), 312 (9), 297 (9), 296 (16), 283 (100), 270 (45), 269 (48), 255 (16), 254 (19), 240 (21), 220 (32), 206 (76).

Starting with **1f** (340 mg, 0.8 mmol), 37 mg (29%) of **4c**, 4.5 mg of (3%) **2f**, and 158 mg of unreacted **1f** were separated. Compound **2f** was identical with our previous sample prepared by direct para–ortho′ phenolic coupling, see ref 16.

Preparation of (±)-Pallidine (4a). *N*-Formylnorisosalutaridine (**4c**) (14 mg, 0.04 mmol) was dissolved in methanol (2 mL) and 18% aqueous hydrogen chloride (0.5 mL). The reaction mixture was kept at 50 °C for 24 h under an argon atmosphere and then the methanol was removed under reduced pressure. The residue was basified with ammonium hydroxide and extracted with dichloromethane. The combined organic layer was dried and evaporated. The crude (±)-norisosalutaridine was purified by preparative TLC (dichloromethane–methanol (100:10, v/v) system with initial ammonia treatment), and N-methylated immediately with 98% formic acid (0.5 mL) and 38% aqueous formaldehyde solution (0.5 mL) (1 h reflux). The reaction mixture was basified with ammonium hydroxide and then extracted with dichloromethane. The organic layer was dried and evaporated. The remaining material was finally purified by preparative TLC (dichloromethane–methanol (150:12, v/v) system with initial ammonia treatment) to supply (±)-pallidine (**4a**) (2.2 mg, 16%), the spectral data of which correspond to those reported earlier[13] for the natural product, which does not separate from an authentic sample on TLC.[23]

Acknowledgment. We thank the CHINOIN Pharmaceutical and Chemical Works (Budapest) for financial support, E. Baitz-Gâcs for ^1H and ^{13}C NMR spectra, and J. Tamâs for the MS measurements.

Registry No. (±)-**1b**, 55869-76-6; (±)-**1c**, 72274-71-6; (±)-**1e**, 72258-92-5; (±)-**1f**, 72264-51-8; (±)-**2c**, 87167-77-9; (±)-**2f**, 87265-23-4; (±)-**3b**, 87332-78-3; (±)-**3c**, 88765-44-0; (±)-**4a**, 27841-88-9; (±)-**4b**, 37729-28-5; (±)-**4c**, 88996-27-4; (±)-norisosaletaridine, 89063-54-7; manganese tris(acetonylacetonate), 14284-89-0; vanadyl bis(acetonylacetonate), 3153-26-2.

(23) Special thanks are expressed to Prof. M. Shamma, The Pennsylvania State University, who was kind enough to provide us with a sample of natural pallidine.

Chlorine Migration in the Mass Spectra of *tert*-Butyldimethylsilyl Derivatives of Chloro Alcohols

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In the course of synthetic studies toward a nitrogen analogue of phyllanthocin,[1] the aglycon of the antileukemic glycoside phyllanthoside, we needed to introduce a hydroxybutyl group. We chose to accomplish this via an organometallic reagent derived from the *tert*-butyldimethylsilyl ether of 4-chlorobutanol. Mass spectral analysis of this latter intermediate revealed an interesting skeletal rearrangement in which chlorine migrated to silicon.

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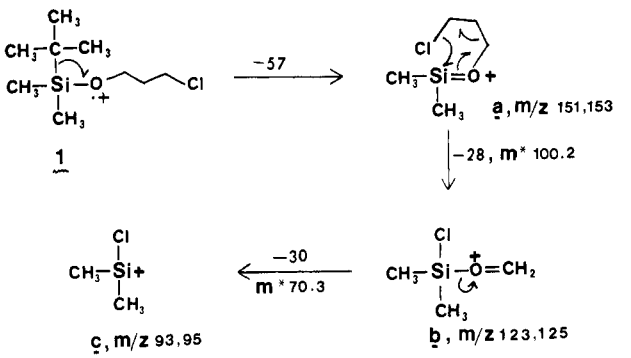
Scheme I



Scheme II

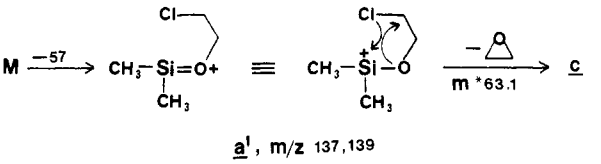


Table I. $\%\Sigma_{40}$ (Relative Intensity) Values for $(CH_3)_3CSi(CH_3)_2O(CH_2)_nCl$

n	M − 57	*m/z* 123 (ion b)	*m/z* 93 (ion c)
2	3.88 (12.1)	0.35 (1.1)	32.16 (100)
3	2.37 (10.5)	9.37 (41.6)	22.53 (100)
4	0.23 (1.5)	13.20 (84.5)	15.61 (100)
5	not detected	5.85 (18.6)	8.66 (27.5)

Mass spectral migrations of various groups to silicon are not without precedence,[2-5] but since the *tert*-butyldimethylsilyl group is so widely used as a blocking group in synthetic organic chemistry we felt that further studies were warranted. Therefore, we prepared a series of *tert*-butyldimethylsilyl-blocked chloro alcohols and found that this halogen to silicon migration is a common process in their electron-impact mass spectra.

The *tert*-butyldimethylsilyl ethers of 2-chloroethanol, 3-chloropropanol, 4-chlorobutanol, and 5-chloropentanol[6] were prepared by reacting the corresponding chloro alcohol with *tert*-butyldimethylsilyl chloride and imidazole in DMF.[7] Using the 3-chloropropanol derivative **1** as a model, we envisage the fragmentations shown in Scheme I as a plausible route to the major ions a–c. These fragmentations are analagous to the deuterium migration to silicon observed with trimethylsilyl ethers of variously deuterated 1-pentanols.[2] Furthermore, metastable ions at *m/z* 100.2 and 70.3 were observed for the transformations a → b and b → c, respectively. Confirmation of the composition of ions a–c was made by high-resolution mass spectroscopy.[8]

In all cases studied the ions resulting from chlorine migration to silicon were prominent (see Table I), except

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(6) 5-Chlorpentanol was prepared by transesterification of 5-chloropentyl acetate with methanol; Fusari, S. A.; Greenlee, K. W.; Brown, J. B. *J. Am. Oil Chem. Soc.* **1951**, *28*, 416.
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(8) Ion a, $C_5H_{12}ClOSi$, *m/z* 151.0340 (calcd 151.0346); ion b, C_3H_8ClOSi, *m/z* 123.0035 (calcd 123.0032); ion c, C_2H_6ClSi, *m/z* 92.9942 (calcd 92.9927).

0022-3263/84/1949-1441$01.50/0