α-Phosphoryl Sulfoxides. 4. Pummerer Rearrangements of α-Phosphoryl Sulfoxides and Asymmetric Induction in the Transfer of Chirality from Sulfur to Carbon[1]

Marian Mikołajczyk,* Andrzej Zatorski, Sławomir Grzejszczak, Burkhard Costisella,[2] and Wanda Midura

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, 90-362 Łódź, Boczna 5, Poland

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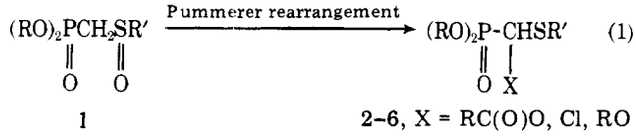
α-Phosphoryl sulfoxides (1) undergo the Pummerer rearrangement, providing an entry into various α-substituted α-phosphirylmethyl methyl(aryl) sulfides. Acetic and trifluoroacetic anhydrides convert α-phosphoryl sulfoxides (1) to the corresponding α-acetoxy- and α-trifluoroacetoxy-α-phosphorylmethyl sulfides. The reaction of sulfoxides I with benzoyl chloride affords α-chloro-α-phosphorylmethyl sulfides. A new method is also described for the synthesis of the *O,S*-thioacetals of formyl phosphonates which involves reaction of sulfoxides 1 with alcohols in the presence of iodine. Reaction of optically active dimethylphosphorylmethyl *p*-tolyl sulfoxide with acetic anhydride was found to result in asymmetric induction at the α-carbon atom in the corresponding α-acetoxy sulfide formed.

The reaction between acid anhydrides and sulfoxides bearing at least one α hydrogen, first discovered by Pummerer,[3] leads to the formation of α-acyloxy sulfides. This and related reactions have attracted considerable attention both from synthetic and mechanistic points of view.[4] It is now commonly accepted that the Pummerer reaction is a complex process which consists of three main steps (Scheme I), i.e., the formation of the acyloxysulfonium salt (A) and then sulfonium ylide (B) which in the last step undergoes the rearrangement to give the final reaction products.

The migration of the acyloxy group from sulfur to the α-carbon atom may occur inter- or intramolecularly depending on the structural effects in the starting sulfoxide.

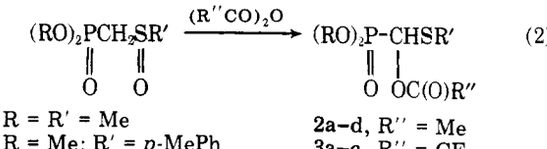


As part of a continuing study of α-phosphoryl sulfoxides (1), which recently became readily available in racemic[5] and optically active forms,[6] we have investigated their various Pummerer-type reactions. Generally, the Pummerer rearrangement of α-phosphoryl sulfoxides (1) results in the formation of α-substituted α-phosphorylmethyl sulfides. Since the latter compounds possess a relatively acidic hydrogen linked to the phosphonate carbon atom they may be utilized further as intermediates in the Horner PO–olefination reaction.[7]

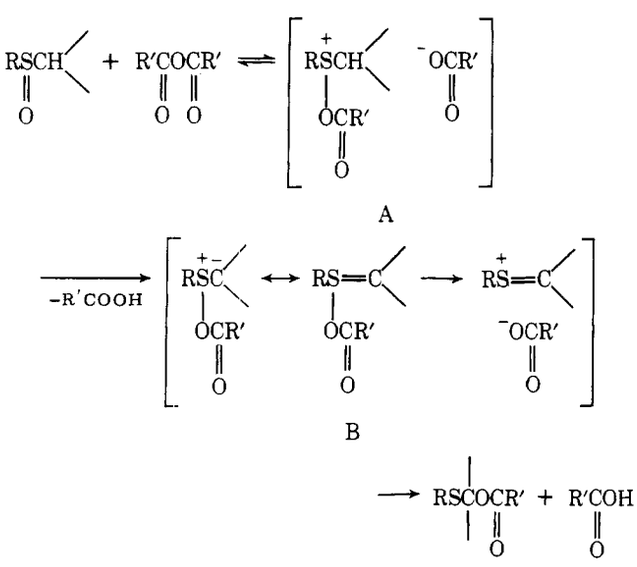
In this paper we present details of several synthetically useful Pummerer-type reactions of α-phosphoryl sulfoxides as well as describe a new example of asymmetric induction in the reaction between optically active dimethylphosphorylmethyl *p*-tolyl sulfoxide and acetic anhydride.

Results and Discussion

Reaction of Racemic and Optically Active α-Phosphoryl Sulfoxides (1) with Carboxylic Acid Anhydrides. First the classical Pummerer reaction of α-phosphoryl sulfoxides (1) with carboxylic acid anhydrides was investigated (eq 2). These reactions, which were performed in refluxing



Scheme I



acetic anhydride, occurred quantitatively in 2–3 h as determined by a periodic assay of the ^{31}P-NMR spectra. The analytically pure α-acetoxy-α-phosphorylmethyl methyl(aryl) sulfides (2) were isolated by distillation or column chromatography on silica gel.

With the more reactive trifluoroacetic anhydride[9] the Pummerer reaction of 1 was complete after 15 min at −78 °C. The resulting α-trifluoroacetoxy-α-phosphorylmethyl methyl(aryl) sulfides (3) were isolated by distillation with the exception of sulfide **3b** which was purified by column chromatography. Physical properties for compounds 2 and 3 are summarized in Table I.[8]

The conversion of sulfoxides into α-acyloxy sulfides is especially interesting from the stereochemical point of view since the chirality at sulfur in transferred to the α carbon. Therefore, the generation of an optically active α-carbon center can be expected when an optically active sulfoxide is used as starting material. Allenmark[10] was the first who observed such asymmetric induction in the reaction of optically active *o*-carboxyphenyl benzyl sulfoxide with acetic anhydride

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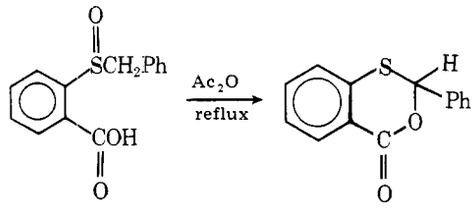
Table I. Preparation and Properties of α-Substituted α-Phosphorylmethyl Sulfides

Product No.	Structure	Registry no.	Reaction conditions Temp (°C)/time	Yield[a] %	n_D (°C) bp (°C)/Torr	^{31}P NMR ($CDCl_3/H_3PO_4$)[b]
2a	$(MeO)_2P(O)CH(OAc)SMe$	65915-08-4	120/2 h	90	1.4700 (26)	+16.4
2b	$(MeO)_2P(O)CH(OAc)STol$	65956-51-6	120/3 h	84	1.5420 (21)	+16.7
2c	$(EtO)_2P(O)CH(OAc)SMe$	65915-09-5	120/2 h	86	1.4570 (23) 85/0.1	+14.3
2d	$(EtO)_2P(O)CH(OAc)SPh$	65956-52-7	120/3 h	88	1.5130 (26)	+14.0
3a	$(MeO)_2P(O)CH(OCOCF_3)SMe$	65915-10-8	−78/15 min	74	1.4050 (22) 62/1.5	+13.9
3b	$(MeO)_2P(O)CH(OCOCF_3)STol$	65915-11-9	−78/15 min	72	1.4663 (23)	+13.7
3c	$(EtO)_2P(O)CH(OCOCF_3)SMe$	65915-12-0	−78/15 min	76	1.3925 (22) 65/0.4	+11.4
4a	$(MeO)_2P(O)CH(Cl)SMe$	65915-13-1	rt[c]/5 h	84	1.4960 (23) 81/0.01	+16.2
4c	$(EtO)_2P(O)CH(Cl)SMe$	65915-14-2	rt[c]/5 h	90	1.4850 (23) 88/0.01	+14.3
4d	$(EtO)_2P(O)CH(Cl)SPh$	65915-15-3	rt[c]/5 h	82	1.5330 (24)	+14.6
6a	$(MeO)_2P(O)CCl_2SMe$	65915-16-4	0/2 h	90	1.5040 (25)	+9.8
6c	$(EtO)_2P(O)CCl_2SMe$	28975-75-9	0/2 h	92	1.4931 (25)	+7.7
6d	$(EtO)_2P(O)CCl_2SPh$	65915-17-5	0/2 h	88	1.5410 (25)	+8.1
7a	$(MeO)_2P(O)CH(OMe)SMe$	65915-18-6	Reflux/2 h	70	1.4652 (22) 58/0.1	+18.0
7b	$(MeO)_2P(O)CH(OMe)STol$	65915-19-7	Reflux/7 h	65	1.5335 (22)	+17.5
7c	$(EtO)_2P(O)CH(OMe)SMe$	65915-20-0	Reflux/1.5 h	82	1.4622 (24) 64/0.1	+16.5
7d	$(EtO)_2P(O)CH(OMe)SPh$	65956-98-1	Reflux/4 h	68	1.5250 (20) 125–8/0.05	+15.0
8c	$(EtO)_2P(O)CH(OEt)SMe$	65915-21-1	Reflux/15 min	73	1.4570 (24) 103–5/1.5	+16.1
8d	$(EtO)_2P(O)CH(OEt)SPh$	65915-22-2	Reflux/50 min	78	1.5270 (20) 138–142/0.02	+16.0

[a] Isolated yield of purified product. Satisfactory analytical data (±0.4% for C, H, P) were reported for all new compounds listed in the table. [b] In this paper the new convention of positive ^{31}P-NMR signals to low field from H_3PO_4 is used. [c] Room temperature.

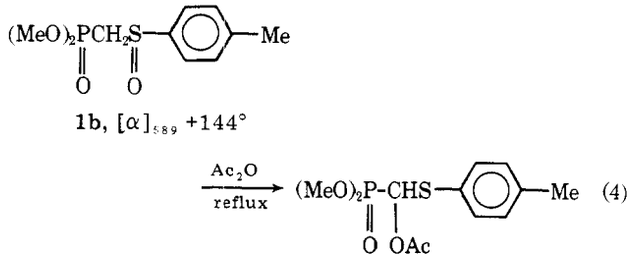
to give the cyclic optically active product, 3,1-benzoxathian-4-one (eq 3).



(3)

$[\alpha]_{589}$ +451° $[\alpha]_{589}$ +17.3° (ee 11.2%)

Since optically active dimethylphosphorylmethyl *p*-tolyl sulfoxide (**1b**) has become readily available,[6] it was of interest to investigate its Pummerer rearrangement in the hope of observing a new example of asymmetric induction in the transfer of chirality from sulfur to α carbon. In fact treatment of sulfoxide **1b**, $[\alpha]_{589}$ + 144°, with excess acetic anhydride at 120 °C for 2 h afforded optically active α-acetoxy-α-(dimethylphosphoryl)methyl *p*-tolyl sulfide (**2b**) having $[\alpha]_{589}$ −4° (eq 4). This value of optical rotation corresponds to 24%

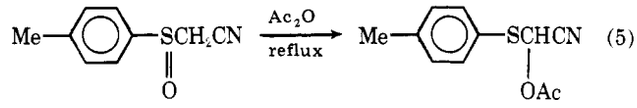


1b, $[\alpha]_{589}$ +144°

(4)

2b, $[\alpha]_{589}$ −4° (ee 24%)

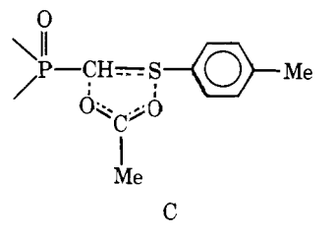
of optical purity at the chiral carbon center in **2b** as determined by means of ^1H-NMR spectroscopy using the chiral lanthanide shift reagent, tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium.[11] The best separation of enantiomeric resonances of **2b** was observed for the methine proton which permitted accurate integration and determination of the enantiomeric purity. After this work was completed Oae and Numata[12] reported asymmetric induction in the Pummerer reaction of optically active α-cyanomethyl *p*-tolyl sulfoxide (eq 5).



(5)

$[\alpha]_{589}$ +252° $[\alpha]_{589}$ +26.8° (ee 29%)

It should be noted that the methylene group of **1b** is highly activated because of the presence of the highly electron withdrawing phosphoryl and sulfinyl groups. Therefore, it is reasonable to assume that proton removal should be fast and reversible,[13] whereas the 1,2 shift of the acetoxy group is likely to be rate determining (Scheme I). The observation of substantial asymmetric induction strongly suggests that acetoxy

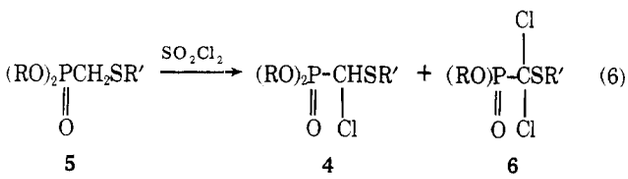


C

migration occurs to a large extent by an intramolecular process presumably via a five-membered cyclic transition state such as C. Additional studies regarding the mechanism of the Pummerer reaction using asymmetric substrates are under way.

Reaction of α-Phosphoryl Sulfoxides (1) with Acid Chlorides. We next investigated the reaction of sulfoxides 1 with acid chlorides which have also been used to initiate Pummerer rearrangements. In this case α-chloro-α-phosphorylmethyl methyl(aryl) sulfides (4) should result. It is worth pointing out that these compounds are potential precursors of the corresponding α-phosphoryl carbanions or carbenes.

A synthesis of α-chloro sulfides (4) by direct chlorination of α-phosphoryl sulfides (5) by means of sulfuryl chloride was reported by Gross et al.[14] (eq 6). However, careful examination

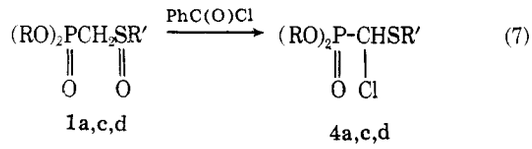


(6)

5 4 6

of this process using ^{31}P-NMR spectroscopy revealed that, although 4 clearly predominates, there is always formed a mixture of monochlorosulfide 4 and dichloro sulfide 6.

Our preliminary attempts to convert α-phosphoryl sulfoxides (1) into the corresponding sulfides 4 by means of acetyl chloride or thionyl chloride were only partly successful since the formation of dichloro sulfides 6 was also observed. For example, reaction of sulfoxide 1c with acetyl chloride afforded a mixture containing 90% 4c and 10% 6c while thionyl chloride gave 87% 4c and 13% 6c. On the other hand, benzoyl chloride, which is less reactive than acetyl chloride, leads to quantitative formation of the desired α-chloro-α-phosphorylmethyl sulfides (4) as shown by the ^{31}P-NMR spectroscopy (eq 7). The

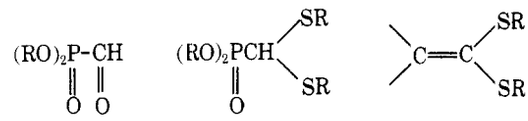


(7)

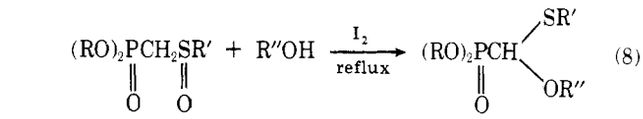
1a,c,d 4a,c,d

results are collected in Table I. For comparison purpose, we also prepared the dichloro sulfides 6 from α-phosphoryl sulfides (5) and 2 mol of sulfuryl chloride.

Synthesis of *O,S*-Thioacetals of Formyl Phosphonates. In a previous paper[15] devoted to α-phosphoryl-substituted organosulfur compounds we described simple methods for the preparation of the *S,S*-thioacetals of formyl phosphonates and their conversion[16] under Horner–Wittig reaction conditions into the corresponding ketene thioacetals which are key intermediates in a wide variety of organic syntheses.



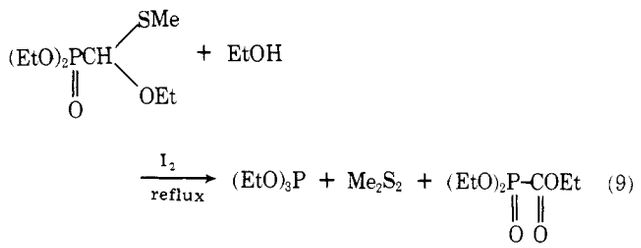
We now wish to report an efficient general synthesis of the *O,S*-thioacetals of formyl phosphonates, which represent a new class of compounds derived from formyl phosphonates. In contrast to the parent formyl phosphonates, which are practically unknown, these compounds are chemically stable and can be easily obtained by the Pummerer-type reaction between α-phosphoryl sulfoxides (1) and alcohols in the presence of iodine (eq 8). This reaction was based on the analogous reaction of β-keto sulfoxides which results, however, in the formation of α-keto acetals.[17]



(8)

1a–d 7a–d, R″ = Me; 8c,d, R″ = Et

Usually, these rearrangements were carried out under reflux in an excess of alcohol using equimolar amounts of iodine. All the reactions have been optimized with regard to yield and purity by ^{31}P-NMR spectroscopy. Results are summarized in Table I. Maintaining optimum reaction times was important since prolonged heating resulted in the formation of various by-products such as trialkyl phosphates, disulfides, dialkyl alkoxycarbonylphosphonates and the *O,O*-acetals or *S,S*-thioacetals of formyl phosphonates. These by-products undoubtedly arise from the further transformations of the *O,S*-thioacetals 7 and 8 under the reaction conditions. As an example, thioacetal 8c has been found to give triethyl phosphate, dimethyl disulfide, and diethyl ethoxycarbonylphosphonate[18] when refluxed in ethanol in the presence of iodine (eq 9).



(9)

Finally, it should be noted that the structures of all compounds synthesized in the present work have been confirmed by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. In a majority of cases we observed in the ^{1}H- and ^{13}C-NMR spectra magnetic nonequivalence of the P-methoxy groups due to the presence of the chirality center on the α-carbon atom. The most characteristic coupling constants $^{2}J_{CH-P}$ and $^{1}J_{^{13}C-P}$ are in the range 10–12.5 Hz and 162–188 Hz, respectively. Appropriate spectral data are given in Table II.

Experimental Section

All boiling points are uncorrected. Solvents and commercial reagents were distilled and dried by conventional methods before use. ^{1}H-NMR spectra were recorded at 60 MHz with a R 12 B Perkin-Elmer spectrometer. ^{31}P- and ^{13}C-NMR spectra were obtained on a Jeol FX-60 F.T. spectrometer with external 85% H_3PO_4 and internal Me_4Si as standards. Column chromatography was carried out on silica gel Meck 100–200 mesh. Optical activity measurements were made with a Perkin-Elmer 241MC photopolarimeter in acetone solution.

Reaction of α-Phosphoryl Sulfoxide (1 with Acetic Anhydride. General Procedure. Sulfoxide 1 (0.01 mol) was dissolved in 10 mL of acetic anhydride and refluxed for 2–3 h at 120 °C. After removal of acetic anhydride and acetic acid under reduced pressure the crude product 2 obtained in 100% yield was purified by distillation or column chromatography.

Reaction of α-Phosphoryl Sulfoxide (1) with Trifuloroacetic Anhydride. General Procedure. Sulfoxide 1 (0.05 mol) and trifluoroacetic anhydride (3 mL) were mixed at −78 °C. The reaction mixture was stirred at this temperature for 15 min. The temperature was then raised to 20 °C and the resulting mixture was evaporated to give crude 3 in quantiative yield. An analytically pure sample of 3 was obtained by distillation or column chromatography.

Reaction of Optically Active Dimethylphosphorylmethyl *p*-Tolyl Sulfoxide (1b) with Acetic Anhdyride. A mixture of sulfoxide **1b** 0.26 g, 0.001 mol), $[\alpha]_{589}$ +144° (97% ee), and acetic anhydride (1 mL) was refluxed for 2 h at 120 °C. Removal of excess acetic anhydride and acetic acid afforded the crude product **2b** which was chromatographed [benzene/acetone, 20:1] to give the analtyically pure α-acetoxy-α-dimethylphosphorylmethyl *p*-tolyl sulfide (**2b**); 0.22 g (73%); $[\alpha]_{589}$ −4° (*c* 3.5, acetone); n^{23}_{D} 1.5230; $\delta_{^{31}P}$ +16.7. Anal. Calcd for $C_{12}H_{17}O_5PS$: C, 47.25; H, 5.62; P, 10.7. Found: C, 47.36; H, 5.63; P, 10.18.

Reaction of α-Phosphoryl Sulfoxide (1) with Benzoyl Chloride. General Procedure. Sulfoxide 1 (0.01 mol) and benzoyl chloride (5 mL) were stirred at room temperature for 5 h. An excess of benzoyl chloride was removed in vacuo and the residue was chromatographed to give chloro sulfide **4**.

Synthesis of α,α-Dichloro-α-phosphorylmethyl Alkyl(aryl) Sulfide (6). General Procedure. α-Phosphoryl sulfoxide (**6**) (0.01 mol) in methylene chloride (25 mL) was treated with sulfuryl chloride (0.022 mol) at 0 °C for 2 h. The solvent and hydrogen chloride were evaporated to give the crude dichloro sulfide (**6**) which was isolated by distillation.

Synthesis of *O,S*-Thioacetals of Formyl Phosphonates 7 and 8. General Procedure. α-Phosphoryl sulfoxide (1) (0.01 mol) was refluxed in an excess of alcohol in the presence of equimolar amounts of iodine. The optimal reaction time, as given in Table I, was estimated by ^{31}P NMR. After the reaction was complete excess alcohol was removed and chloroform was added. The organic solution was washed with thiosulfate solution followed by water, dried, and evaporated. The residue was fractionated or chromatographed to afford pure thioacetal **7** or **8**.

Registry No.—**1a**, 65915-23-3; **1b**, 63231-19-6; (+)-**1b**, 63231-19-6; **1c**, 65915-24-4; **1d**, 65915-25-5; (−)-**2b**, 65915-26-6; **5a**, 25508-32-1; **5c**, 28460-01-7; **5d**, 38066-16-9.

Supplementary Material Available: Table II including full ^{1}H- and ^{13}C-NMR data of **2**–' (4 pages). Ordering information is given on any current masthead page.

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Intramolecular Nonphenol Oxidative Coupling of Phenethylisoquinolines

S. Morris Kupchan,[1] Om P. Dhingra,*[2] Chang-Kyu Kim, and Venkataraman Kameswaran

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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Anodic and chemical oxidative coupling of homolaudanosine (**6a**) in TFA–TFAA gave homoglaucine (**9a**) in moderate yield. Oxidative coupling of *N*-acyl nonphenolic phenethyltetrahydroisoquinolines **6c,e,f** using VOF_3–TFA–TFAA yielded homoproerythrinadienones **8a,c** as the primary products, in contrast to the results of oxidative coupling reactions of nonphenolic benzyltetrahydroisoquinoline precursors which yield morphinandienones as the primary products. Furthermore, the homoproerythrinadienone-type intermediates (e.g., **19**) and homoneospirenedienone-type intermediates (e.g., **20**) were shown to be in equilibrium in the reaction medium, and both spirodienone intermediates rearranged to homoaporphines. Thus the oxidative coupling of nonphenolic phenethyltetrahydroisoquinolines with VOF_3–TFA–TFAA provides an efficient synthetic route to homoproerythrinadienones, homoneospirenedienones, and homoaporphines. Diaryl derivatives such as **11a,b** were also obtained as byproducts, which could be transformed to dibenz[*d*,*f*]azecine (**14a**).

Intramolecular phenol oxidative coupling reactions as a mode of carbon–carbon bond formation hold a prominent position in the biosynthesis of many classes of natural products.[3–5] However, the synthetic potential of these reactions has been limited due to the low yields and the complex mixtures of products usually encountered when the coupling step is carried out in the laboratory.[6,7] Recent reports[8–16] have demonstrated that intramolecular nonphenol oxidative coupling reactions hold promise as effective synthetic methods for the preparation of certain alkaloids and other polycyclic compounds. The first practical synthesis of this type involved electrooxidative coupling of nonphenolic benzylisoquinolines to morphinandienones.[8–11] Chemical intramolecular coupling of nonphenolic benzylisoquinolines using vanadium oxytrifluoride (VOF_3) in trifluoroacetic acid (TFA) also proceeded via morphinandienone intermediates[13–15] to give aporphines and some other spirodienone products. The present paper describes, in detail, studies[17] on the intramolecular oxidative coupling of nonphenolic phenethyltetrahydroisoquinoline derivatives which represent efficient syntheses of homoproerythrinadienones, homoneospirenedienones, homoaporphines, and dibenz[*d*,*f*]azecine precursors.

On the basis of the results of oxidative couplings of nonphenolic benzyltetrahydroisoquinolines,[8,13,14] it seemed reasonable to assume that anodic coupling of nonphenolic phenethyltetrahydroisoquinolines would yield homomorphinandienones, and VOF_3–TFA oxidations would give homoaporphines and homoneospirenedienones (Scheme I). Thus, homolaudanosine (**6a**) seemed a reasonable starting material for initial studies. Preparation of homolaudanosine

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