Synthesis of 1,2- and 1,3-Divinylpyrrole

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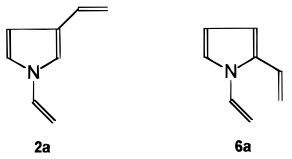
Vinylpyrroles having the double bond conjugated to the heteroaromatic ring represent a very important heterocycles class. They are synthons to indole ring systems via Diels−Alder reaction with various active dienophiles[1] as well as bifunctional monomers for the preparation of conducting and nonlinear optics materials.[2] Despite the great interest in their use, these compounds have been until now poorly utilized, both their instability and the difficulty of preparing 3-substituted derivatives likely being a consistent limitation.

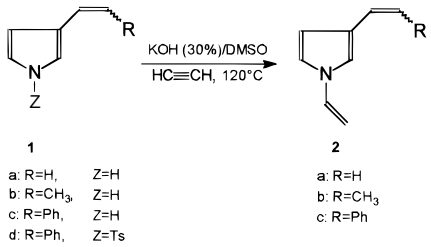
We first reported[3] that 3-vinylpyrroles can be prepared from pyrrole according to simple general methods and they can be easily handled at room temperature. Successively a similar procedure has been used by Ketcha[4] et al., while Wang[5] et al. reported the synthesis of some 3-vinylpyrroles substituted on the aromatic ring by the Stille coupling reaction. Recently we demonstrated that the three vinylpyrrole isomers as well as the 2- and 3-vinylpyrrole N-tosylated can be submitted to rhodium-catalyzed hydroformylation conditions without any decomposition, conveniently giving 2-pyrrolylpropanals.[6] Owing to our interest into the hydroformylation of vinyl heteroaromatic substrates[6,7] and on the basis of our experience in the synthesis of vinylpyrrolyl derivatives,[3] it seemed a very attractive challenge to try the preparation and to test the reactivity of the divinylpyrroles, a heterocycles class of compounds unknown in the literature.

We report here that 1,3-divinylpyrrole (**2a**) and 1,2-divinylpyrrole (**6a**) (Chart 1) can be conveniently prepared by the procedures depicted in the Schemes 1 and 2. **2a** was prepared by direct N-vinylation with acetylene of the corresponding 3-vinylpyrrole (**1a**) (Scheme 1). 1,2-Divinylpyrrole (**6a**) was obtained from 2-formylpyrrole (**3a**) via indirect N-vinylation (N-chloroethylation/dehydrochlorination) followed by Wittig methylenation of the formyl group (Scheme 2). Analogous procedures (Schemes 1−3) allowed the synthesis of the related compounds **2b**−**c**, **6b**,[8] and **10**.

Chart 1



Scheme 1



Results

Direct N-vinylation of 3-Alkenylpyrroles: Preparation of the 1,3-Divinylpyrroles 2a−c (Scheme 1). (a) 1,3-Divinylpyrrole (2a). 2a was prepared by treatment of the corresponding 3-vinylpyrrole (**1a**)[3a] with acetylene, in KOH (30%)/DMSO, at 120 °C, according to the "superbasic" Trofimov's conditions[9b] (Scheme 1). The reaction was conveniently carried out under acetylene pressure (10 atm) in a stainless autoclave for 2 h. Then the recovered mixture was added to brine and extracted with dichloromethane. After evaporation of the solvent, 1,3-divinylpyrrole was obtained as a yellow dense liquid (55% yield) by distillation at reduced pressure. **2a** is stable enough to be stored at 0 °C for some weeks without significative decomposition.

(b) 1,3-Divinylpyrroles *β*-Substituted in the 3-Vinyl Group (2b,c). The same procedure (Scheme 1) afforded also the 1,3-divinypyrrole analogues, namely 3-(1-propenyl)-1-vinylpyrrole (80:20 trans/cis mixture) (**2b**) and 3-(2-phenylethenyl)-1-vinylpyrrole (as trans isomer) (**2c**), respectively, from the corresponding 3-(1-propenyl)pyrrole (**1b**)[3a] and 3-(2-phenylethenyl)pyrrole (**1c**).[3a] The N-vinylation occurs without variation of the cis/trans ratio, the products **2b**,**c** showing the same regioisomeric content observed in the starting N-unsubstituted substrates. Isolation of **2b**,**c** was accomplished by liquid chromatography on a silica gel column, by

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(1) (a) For a review about indole ring synthesis, see: Gribble, G. W. *Contemp. Org. Synth*. **1994**, *1*, 145. (b) Jones, R. A.; Aznar-Saliente, T.; Sepulveda-Arques, J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2451. (c) Ohno, M.; Shimizu, S.; Eguchi, S. *Tetrahedron Lett.* **1990**, *31*, 4613. (d) Keil, J. M.; Kampchen, T.; Seitz, G. *Tetrahedron Lett.* **1990**, *31*, 4581. (e) Hodges, L. M.; Moody, M. W.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 7931.

(2) (a) Alagona, G.; Ghio, C.; Cavazza, M.; Nucci, L.; Pergola, F.; Colligiani, A. *Synth. Met.* **1994**, *67*, 235. (b) Niziurski-Mann, R. E.; Cava, M. P. *Heterocycles* **1992**, *34*, 2003. (c) Naarmann, H.; Theophilou, N. In *Electroresponsive Molecular and Polymeric Systems*; Marcel Dekker Inc.: New York, 1988; Vol. 1. (d) Bauerle, P. *Adv. Mater*. **1993**, *5*, 879.

(3) (a) Settambolo, R.; Lazzaroni, R.; Messeri, T.; Mazzetti, M.; Salvadori, P. *J. Org. Chem*. **1993**, *58*, 7899. (b) Settambolo, R.; Mazzetti, M.; Pini, D.; Pucci, S.; Lazzaroni, R. *Gazz. Chim. Ital*. **1994**, *124*, 173.

(4) Xiao, D.; Ketcha, D. M. *J. Heterocycl. Chem*. **1995**, *32*, 499.

(5) Wang, J.; Scott, A. I. *Tetrahedron Lett*. **1995**, *39*, 7043.

(6) (a) Settambolo, R.; Caiazzo, A.; Lazzaroni, R. *J. Organomet. Chem*. **1996**, *506*, 337. (b) Settambolo, R.; Caiazzo, A.; Lazzaroni, R. *Synth. Commun*. **1997**, *27*, 4111.

(7) (a) Settambolo, R.; Pucci, S.; Bertozzi, S.; Lazzaroni, R. *J. Organomet. Chem*. **1995**, *489*, C50. (b) Caiazzo, A.; Settambolo, R.; Uccello-Barretta, G.; Lazzaroni, R. *J. Organomet. Chem*. **1997**, *548*, 279.

(8) Trofimov, B. A.; Oleinikova, E. B.; Sigalov, M. V.; Skvortsov, Yu. M.; Mikhaleva, A. I. *Zh. Org. Khim*. **1980**, *16*, 410.

(9) (a) Trofimov, B. A. In *The Chemistry of Heterocyclic Compounds;* John Wiley and Sons Inc.: New York, **1992**; Vol. 48. (b) Tarasova, O. A.; Mal'kina, A. G.; Mikhaleva, A. I.; Brandsma, L.; Trofimov, B. A. *Synth. Commun*. **1994**, *24*, 2035.

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eluting with a 10:1 hexane/EtOAc mixture and 1:1 benzene/hexane mixture, respectively.

Interestingly **2c** has been also obtained directly from the corresponding 3-(2-phenylethenyl)-1-tosylpyrrole (**1d**) (Scheme 1), precursor of 3-(2-phenylethenyl)pyrrole (**1c**),[3a] by treatment of **1d** with acetylene in KOH (30%)/DMSO, the N-detosylation and the N-vinylation occurring in "one pot".

As observed for 1,3-divinylpyrrole, the new compounds **2b**,**c** are stable at low temperatures, although they are quite unstable at room temperature.

Indirect N-Vinylation of 2- and/or 3-Acylpyrroles: Preparation of the 1,2-Divinylpyrroles 6a,b (Scheme 2) and of 3-(1-Methylethenyl)-1-vinylpyrrole (10) (Scheme 3). (a) 1,2-Divinylpyrrole (6a). 6a was prepared in two steps by dehydrohalogenation of 1-(2-chloroethyl)-2-formylpyrrole (**4a**) to give 2-formyl-1-vinylpyrrole (**5a**) followed by Wittig methylenation of the formyl group of **5a**. The intermediate **4a** was obtained, in quantitative yield, by treatment of the commercial pyrrole-2-carboxyaldehyde (**3a**) in 1,2-dichloroethane, both as an organic solvent and a reactant, with 50% aqueous NaOH, under catalytic phase-transfer conditions. Unlike that reported in the literature[10] for the preparation of **4a**, the use of tetrabutylammonium hydrogen sulfate (molar ratio 1:10 with respect to the substrate) resulted to be more convenient than the utilization of tetrabutylammonium iodide, the isolation of the final product being easier and the yield being very good (97%).

The dehydrochlorination of **4a** to give **5a** was accomplished by treatment of **4a** with DBU in anhydrous DMSO at 80 °C. Isolation of **5a**, as a chemically pure yellow oil, was accomplished by liquid chromatography on a silica gel column, by eluting with a 3:1 hexane/AcOEt mixture (80% yield).[11] The Wittig methylenation of **5a** with methyltriphenylphosphonium bromide and sodium amide in THF (molar ratio substrate/ylide = 1:2; reaction time 1 h) provided 1,2-divinylpyrrole, as an oily residue.[12] The isolation of 1,2-divinylpyrrole, as a pure oil (45% yield), was accomplished by distillation at reduced pressure.

It is noteworthy that the same olefin was conveniently prepared from **4a** via N-dehydrohalogenation and methylenation in "one pot", under stressed Wittig conditions (molar ratio substrate/ylide = 1:3; reaction time 7 h) (overall yield 45%). **6a** is stable enough to be distilled without significative decomposition and stable for some weeks at 0 °C.

(b) 2-(1-Methylethenyl)-1-vinylpyrrole (6b). The same reaction sequence adopted for **6a** (Scheme 2) also afforded 2-(1-methylethenyl)-1-vinylpyrrole (**6b**) via formation of 2-acetyl-1-chloroethylpyrrole (**4b**). This compound was prepared (93% yield) on refluxing the commercial 2-acetylpyrrole (**3b**) under the same catalytic phase-transfer conditions adopted for **3a**. The successive reaction of **4b** with DBU in hot DMSO gave 2-acetyl-1-vinylpyrrole (**5b**). Whereas in the case of 2-formyl-1-vinylpyrrole (**5a**) a good yield of the isolated pure product was obtained, the purification of 2-acetyl-1-vinylpyrrole was more difficult, this compound appearing quite unstable during the elution on a silica gel column; nevertheless the saturation of the eluent mixture (5:3 hexane/EtOAc) with NH_3 permitted us to obtain **5b**, as a pale yellow liquid, in 55% yield. The treatment of **5b** under Wittig conditions gave **6b**. Then the isolation of 2-(1-methylethenyl)-1-vinylpyrrole, as a pure colorless liquid, has been accomplished by distillation at reduced pressure. **6b** can be stored at 0 °C without any decomposition for some weeks.

Unlike that observed for the analogous 1-chloroethyl-2-formylpyrrole (**4a**), the intermediate **4b** was not directly transformed into 2-(1-methylethenyl)-1-vinylpyrrole (**6b**) with a ylide excess, the desired product being obtained in very low amount together with various unidentified products.[13]

(c) 3-(1-Methylethenyl)-1-vinylpyrrole (10). 10 was prepared from 3-acetylpyrrole (**7**) via N-chloroethylation and N-dehydrohalogenation in "one pot" to give 3-acetyl-1-vinylpyrrole (**9**) followed by Wittig methylenation of the carbonyl group of **9** (Scheme 3). **7** was easily obtained from the corresponding N-tosylated substrate[14] by treatment with 5 M aqueous NaOH in dioxane. In a first attempt to obtain **8**, 3-acetylpyrrole was treated with dichloroethane under the same phase-transfer conditions adopted for **3**: the expected 3-acetyl-1-(2-chloroethyl)-pyrrole (**8**) together with the N-dehydrohalogenation product 3-acetyl-1-vinylpyrrole (**9**) in a 60:40 mixture was obtained. To completely convert the substrate **8** into **9** a longer reaction time was adopted (6 h), but formation of polymeric material was observed too. Finally 3-acetyl-1-vinylpyrrole (**9**) was obtained in "one pot", in good yield of isolated pure product (88%), by heating 3-acetylpyrrole with an excess of NaOH (1:35 substrate/NaOH) and 1,2-dichloroethane, at reflux. The Wittig methylenation of **9** with methyltriphenylphosphonium bromide and sodium amide in THF (Scheme 3) provided 3-(1-methylethenyl)-1-vinylpyrrrole (**10**) as an oily residue, after distillation at reduced pressure (45% yield). **10** is characterized by the same stability shown by the analogous substrates.

Discussion

The synthetic pathways here depicted use two N-vinylation methods previously described in the literature[9,10] but employed in this work for the first time in the synthesis of divinylpyrroles. With respect to the original version, some modifications and improvements have been accomplished by us. As far as the direct N-vinylation is concerned, the reaction was conveniently carried out in a stainless autoclave under acetylene pressure instead of in a glass flash at atmospheric pressure.[9b] In light of our experience in the high-pressure

(10) Gonzalez, C.; Greenhouse, R.; Tallabs, R. *Can. J. Chem.* **1983**, *61*, 1697.

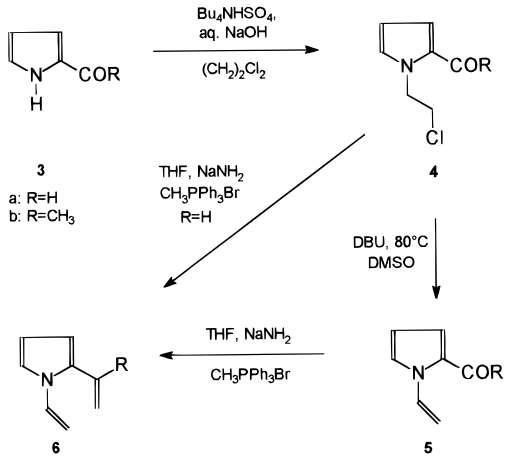
(11) The compound **5a** is prepared in the literature[10] by heating 1-(2-chloroethyl)-2-formylpyrrole with sodium hydride in mineral oil in dry acetonitrile at 50 °C, but no isolation conditions are reported. An analogous attempt to prepare **5a** carried out by us did not give the desired product: indeed, uncharacterized polymeric material was recovered from the reaction mixture as the main product.

(12) The base used in the ylide formation was crucial in order to promote the double transformation: an attempt carried out with the same phosphonium salt and butyllithium base, under analogous experimental conditions, only favored the methylenation of the formyl group but not the N-dehydrohalogenation, affording 1-(2-chloroethyl)-2-vinylpyrrole (40% yield).

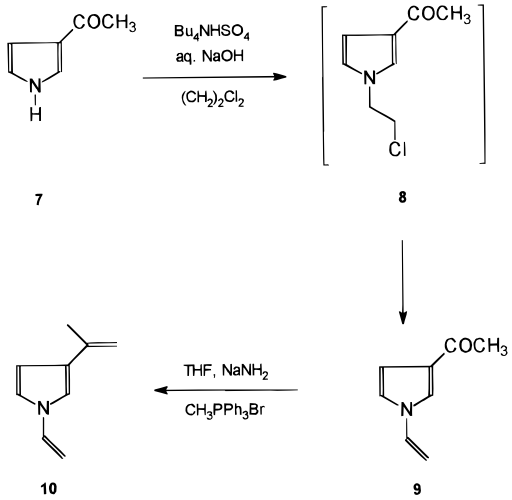
(13) It is likely possible that, under stressed Wittig conditions, there is a competition between the methylenic proton adjacent to the nitrogen atom and the methylic proton adjacent to the carbonyl group: in fact a volatile component (GC-MS control) compatible with a bicyclic structure, generated from the intramolecular substitution of the chloride atom by the carbanion deriving from the methyl group, was detected by GC-MS control.

(14) Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 3214.

Scheme 2



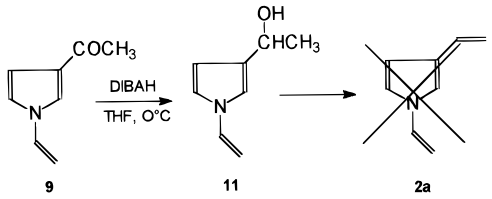
Scheme 3



reactions, we think that the use of an autoclave, when available, ensures high safety and makes easier the operative conditions. An interesting application of this procedure resulted the preparation of 3-(2-phenylethenyl)-1-vinylpyrrole from the corresponding N-tosylated substrate, without preventive N-detosylation. The presence of an electron-withdrawing group in the 3 annular position is crucial in order to obtain "one pot" deprotection and N-vinylation of the substrate; indeed analogous attempts carried out on 3-vinyl-1-tosylpyrrole and 3-(1-propenyl)-1-tosylpyrrole have been unsuccessful, leading mixtures of unreacted substrate, detosylated product, and 3-alkenyl-1-vinylpyrroles in very low amount.

As far as the indirect N-vinylation is concerned, we showed that this procedure can be conveniently applied to 2-acylpyrroles as well as 3-acylpyrroles. In particular in the case of 2-acyl derivatives a convenient N-dehydrohalogenation and methylenation in "one pot" under Wittig conditions was set up in the synthesis of 1,2-divinylpyrrole (Scheme 2). In addition the original N-chloroethylation and N-dehydrohalogenation in "one pot" of 3-acetylpyrrole to give 3-acetyl-1-vinylpyrrole (**9**) proved to be a convenient key intermediate in the preparation of **10**. This last synthetic sequence can constitute, in our opinion, an approach of general utility in the preparation of 3-vinyliden-1-vinylpyrroles, as an alternative route to the direct N-vinylation with acetylene of the corresponding 3-vinylidenpyrroles.[3b]

Scheme 4



The synthesis of **9** being easy and convenient, it seemed interesting to verify if this compound could be used as an intermediate in the preparation of 1,3-divinylpyrrole. The key of the synthetic pathway could be the reduction of the carbonyl group of **9** to hydroxyl group to give **11** and the successive dehydration to obtain a vinyl group in position 3, according to the reaction sequence successfully adopted in the synthesis of 3-alkenylpyrroles from 3-acyl-1-tosylpyrroles.[3] Although 3-(1-hydroxyethyl)-1-vinylpyrrole (**11**) has been obtained in very good yield (>90%) by using diisobutylaluminum hydride in THF, at 0 °C, as a chemoselective reducing system, no attempt to dehydrate **11** gave the desired product[15] (Scheme 4).

Probably the Wittig methylenation of 3-formyl-1-vinylpyrrole could be an alternative synthetic approach to 1,3-divinylpyrrole, but the insertion of a formyl group on 3 annular position is more difficult than the insertion of an acyl group on the same position;[16] hence, this approach is not convenient.

On the basis of that reported for the synthesis of 1,3-divinylpyrroles, the direct N-vinylation of 2-monovinyls was, in principle, a possible way to obtain 1,2-divinylpyrroles. However 2-alkenylpyrroles are not easily available and they are generally obtained in low yield,[17] because of their trend to polymerize. It is noteworthy that 2-vinyl-1-tosylpyrrole has been previously prepared by us in good yield,[6b] but it is not deprotected[17] under the basic hydrolysis conditions successfully adopted for the analogous 3-substituted in the synthesis of 3-alkenylpyrroles: then the indirect N-vinylation of 2-acylpyrroles followed by Wittig reaction seems to be the best way to 1,2-divinylpyrroles.

Conclusions

The synthetic routes herein depicted represent convenient and simple methods for the preparation of 1,2- and/or 1,3-divinylpyrroles from commercially available 2-acylpyrroles and easily synthesizable 3-acylpyrroles and 3-vinylpyrroles. The procedures employ inexpensive reagents and provide pure products after simple purification processes. The newly prepared divinylpyrroles and the various intermediates are stable enough to be handled at room temperature and can be prepared in a consistent scale (hundreds of milligrams). The easy accessibility to the divinylpyrroles suggests the use of these compounds as useful intermediates in various research fields. In particular they could substitute the more investigated

(15) The treatment of **11** with DMSO at 100 °C, previously used in the preparation of 3-alkenylpyrroles from the corresponding 3-(2-hydroxyalkyl)pyrroles,[3] gave polymerization products; under this limit temperature the reaction did not occur. Polymeric material was also obtained by using methanesulfonyl chloride/triethylamine as dehydrating system. A final attempt carried out with hot aqueous NaOH and ethanol gave only traces of the desired product together with unreacted starting substrate.

(16) Demopoulos, V. J. *Org. Prep. Proced. Int.* **1986**, *18*, 278.

(17) Caiazzo, A. Thesis of Laurea, University of Pisa, 1996; p 81.

divinylbenzenes as cross-linking agents in polymerization processes. On the other hand, analogously to that reported for the simple N-vinylpyrrole,[2a] they can be considered polyfunctional precursors to electroconducting organic polymers, being reactive both at the exocyclic double bonds and at positions α to the pyrrole ring. In addition the presence of a C-vinyl group and a N-vinyl group on the same aromatic ring makes the divinylpyrroles interesting substrates in order to study the influence of the vinyl group nature on typical double bond reactions. To this regard, the hydroformylation reaction is now under investigation.

Experimental Section

All reagents were of commercial quality. Schlosser-Schaub "instant ylide" reagent (methyltriphenylphosphonium bromide + sodium amide) was purchased from Fluka. Silica gel (70−230 mesh) was purchased from Merck. DMSO was refluxed and then distilled over calcium hydride. THF was refluxed and distilled over Na/K.

Microanalyses were performed at the Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. ^{1}H NMR spectra (200 MHz) were recorded in $CDCl_3$.

3-Vinylpyrrole (**1a**), 3-(1-propenyl)pyrrole (**1b**), 3-(2-phenylethenyl)pyrrole (**1c**), and 3-(2-phenylethenyl)-1-tosylpyrrole (**1d**) were synthesized as described in the literature.[3a]

1,3-Divinylpyrroles. General Procedure. 1,3-Divinylpyrrole (2a). A mixture of 3-vinylpyrrole (**1a**) (1.5 g, 1.6×10^{-2} mol), KOH (machine-powdered) (1.1 g, 2.9×10^{-2} mol), and anhydrous DMSO (6 mL) was introduced into a stainless steel autoclave equipped with a magnetic stirrer. Acetylene was introduced (10 atm), and the autoclave was then heated to 120 °C for 2 h. After cooling to room temperature, the crude reaction mixture was treated with brine and extracted thoroughly with methylene chloride. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated to give a yellow oil which was distilled at reduced pressure to afford **2a** (1.05 g, 8.8×10^{-3} mol, 55% yield) as a yellowish oil: bp 65 °C, 2×10^{-3} mbar; ^{1}H NMR δ 6.88 (m, 1H), 6.81 (m, 1H), 6.74 (dd, 1H, J = 8.6, 16.0 Hz), 6.57 (dd, 1H, J = 10.8, 18.0 Hz), 6.38 (m, 1H), 5.44 (dd, 1H, J = 1.7, 18.0 Hz), 5.06 (dd, 1H, J = 2.2, 16.0 Hz), 5.00 (dd, 1H, J = 1.7, 10.8 Hz), 4.62 (dd, 1H, J = 2.2, 8.6 Hz); MS *m*/*e* 119 (M^+, 75.8), 104 (7.8), 91 (53.0), 65 (58.8), 51 (26.9), 39 (100). Anal. Calcd for C_8H_9N: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.55; H, 7.65; N, 11.82.

3-(1-Propenyl)-1-vinylpyrrole (2b). This was prepared according to the general procedure except that **1b** (1.2 g, 2.1×10^{-2} mol) was used: yield 1.40 g (1.05×10^{-2} mol, 50% yield) of **2b** as a yellow liquid (SiO_2; 10:1 hexane/EtOAc); ^{1}H NMR δ 6.90−6.70 (m, 3H), 6.37 (m, 1H, trans isomer), 6.30 (m, 1H, cis isomer), 6.05 (m, 1H, trans isomer), 5.97 (m, 1H, cis isomer), 5.80 (m, 1H, trans isomer), 5.12 (d, 1H, J = 16.5 Hz), 4.67 (d, 1H, J = 10 Hz), 1.97 (d, 3H, cis isomer), 1.92 (d, 3H, trans isomer); MS *m*/*e* 133 (M^+, 100), 117 (35.5), 106 (69), 91 (15), 77 (34.5), 65 (19.6), 51 (38). Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.10; H, 8.25; N, 10.60.

3-(2-Phenylethenyl)-1-vinylpyrrole (2c). Method 1. This was prepared according to the general procedure except that **1c** (2.0 g, 1.2×10^{-2} mol) was used: yield 1.17 g (6.0×10^{-3} mol, 50% yield) of **2c** as a yellow solid (SiO_2; 1:1 hexane/benzene): mp 112−113 °C; ^{1}H NMR δ 7.54−6.78 (m, 10 H), 6.57 (m, 1H), 5.18 (d, 1H, J = 15 Hz), 4.72 (d, 1H, J = 10 Hz); MS *m*/*e* 195 (M^+, 100), 180 (7), 167 (22.7), 152 (17.2), 141 (18.6), 115 (25.5). Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.08; H, 6.68; N, 7.25.

Method 2. 2c was also prepared by using the same procedure employed for the N-vinylation described above but with **1d** (0.50 g, 3.0×10^{-3} mol): yield 0.234 g (1.2×10^{-3} mol, 40% yield) of **2c**.

2-Acyl-1-(2-chloroethyl)pyrroles. General Procedure. 1-(2-Chloroethyl)-2-formylpyrrole (4a). A 50% aqueous NaOH (30 mL) solution was added, at 0 °C, to a stirred solution of 2-formylpyrrole (**3a**) (3.0 g, 3.2×10^{-2} mol) and tetrabutylammonium hydrogen sulfate (1.1 g, 3.2×10^{-3} mol) in 1,2-dichloroethane (60 mL). The mixture was then heated to reflux temperature, with vigorous stirring, for 1 h. The cooled mixture was diluted with water and extracted with dichloromethane. The combined organic extracts were washed with water, dried (Na_2SO_4), and evaporated in vacuo to give 4.8 g (3.1×10^{-2} mol, 97% yield) of **4a** as a yellow oil.

2-Acetyl-1-(2-chloroethyl)pyrrole (4b). This was prepared by using the same procedure employed for the N-chloroethylation described above but with **3b** (7.0 g, 6.4×10^{-2} mol) and yielded **4b** (10.2 g; 5.9×10^{-2} mol, 93% yield) as a colorless semisolid: ^{1}H NMR δ 7.02 (m, 1H), 6.95 (m, 1H), 6.17 (m, 1H), 4.60 (t, 2H), 3.82 (t, 2H), 2.45 (s, 3H); MS *m*/*e* 171 (M+, 32), 156 (32), 136 (100), 120 (17.8). Anal. Calcd for $C_8H_{10}NOCl$: C, 55.99; H, 5.87; N, 8.16. Found: C, 55.88; H, 5.96; N, 8.17.

2-Acyl-1-vinylpyrroles. General Procedure. 2-Formyl-1-vinylpyrrole (5a). DBU (3 mL, 2.0×10^{-2} mol) was added to a stirred solution of 1-(2-chloroethyl)-2-formylpyrrole (**4a**) (1.0 g, 6.4×10^{-3} mol) in anhydrous DMSO, heated at 80 °C. After 6 h, the mixture, cooled to room temperature, was diluted with water and extracted with dichloromethane. The combined organic layers were treated with water and dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue which was chromatographed on silica gel, by eluting with 75:25 hexane/EtOAc to afford **5a** (0.62 g, 5.12×10^{-3} mol, 80% yield) as a pale yellow oil: ^{1}H NMR δ 9.60 (s, 1H), 7.94 (dd, 1H, J = 8.8, 15.8 Hz), 7.38 (m, 1H), 6.98 (m, 1H), 6.33 (m, 1H), 5.24 (dd, 1H, J = 1.3, 15.8 Hz), 4.89 (dd, 1H, J = 1.3, 8.8 Hz); MS *m*/*e* 121 (M^+, 100), 106 (40.8), 92 (40), 78 (7), 65 (53). Anal. Calcd for C_7H_7NO: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.50; H, 5.85; N, 11.60.

2-Acetyl-1-vinylpyrrole (5b). This was prepared by using the same procedure employed for the N-dehydrohalogenation described above but with **4b** (4.0 g, 2.3×10^{-2} mol) and yielded **5b** (1.7 g, 1.26×10^{-2} mol, 55% yield), as a pale yellow oil (SiO_2; 5:3 hexane/EtOAc saturated with NH_3): ^{1}H NMR δ 7.97 (dd, 1H, J = 8.8, 15.7 Hz), 7.26 (m, 1H), 7.00 (m, 1H), 6.23 (m, 1H), 5.18 (dd, 1H, J = 1, 15.7 Hz), 4.85 (d, 1H, J = 8.8 Hz), 2.44 (s, 3H); MS *m*/*e* 135 (M^+, 100), 120 (69.3), 107 (14), 92 (84.8), 65 (50). Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.05; H, 6.66; N, 10.45.

3-Acetyl-1-vinylpyrrole (9). To a stirred solution of 3-acetylpyrrole (**7**) (1.2 g, 1.1×10^{-2} mol) and tetrabutylammonium hydrogen sulfate (0.37 g, 1.1×10^{-3} mol) in 1,2-dichloroethane (6 mL), at 0 °C, was added 21 mL of 50% aqueous NaOH. The resulting mixture was refluxed for 1.5 h, allowed to cool, diluted with water, and extracted with methylene chloride. The combined organic extracts were washed with water, dried (Na_2SO_4), and evaporated in vacuo to give a pale yellow residue which was chromatographed on silica gel, by eluting with 3:5 hexane/EtOAc to afford **9** (1.3 g, 9.7×10^{-3} mol, 88% yield) as a colorless oil: ^{1}H NMR δ 7.45 (m, 1H), 6.89 (m, 1H), 6.82 (dd, 1H, J = 15.7, 8.9 Hz), 6.66 (m, 1H), 5.26 (dd, 1H, J = 1.66, 15.7 Hz), 4.85 (dd, 1H, J = 1.66, 8.9 Hz), 2.42 (s, 3H); MS *m*/*e* 135 (M^+, 43), 120 (100), 92 (37), 65 (26), 39 (11). Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.05; H, 6.65; N, 10.42.

1,2-Divinylpyrroles. General Procedure. 1,2-Divinylpyrrole (6a). Method 1. To a stirred mixture of anhydrous THF (20 mL) and Schlosser−Schaub reagent (4.0 g, 9.6×10^{-3} mol of methyltriphenylphosphonium bromide), under a nitrogen atmosphere, a solution of 2-formyl-1-vinylpyrrole (**5a**) (0.580 g, 4.8×10^{-3} mol) in anhydrous THF (12 mL) was added. The reaction mixture was stirred at room temperature for 1 h and then treated with a 50% aqueous solution of NaOH and extracted with ethyl ether. The combined organic extracts were washed with water, dried (Na_2SO_4), and evaporated in vacuo to give a residue which was distilled at reduced pressure to afford **6a** (0.257 g, 2.16×10^{-3} mol, 45% yield) as a yellow oil: bp 30 °C, 2×10^{-3} mbar; ^{1}H NMR δ 6.99 (dd, 1H, J = 8.9, 15.3 Hz), 6.95 (m, 1H), 6.62 (dd, 1H, J = 11.2, 17.4 Hz), 6.37 (m, 1H), 6.20 (m, 1H), 5.50 (dd, 1H, J = 1.46, 17.4 Hz), 5.15 (dd, 1H, J = 1.10, 15.3 Hz), 5.13 (dd, 1H, J = 1.46, 11.2 Hz), 4.76 (d, 1H, J = 8.9 Hz); MS *m*/*e* 119 (M+, 62), 118 (100), 104 (15), 91 (14.3), 65 (11). Anal. Calcd for C_8H_9N: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.62; H, 7.55; N, 11.80.

Method 2. To a stirred mixture of anhydrous THF (40 mL) and Schlosser−Schaub reagent (10.0 g, 2.4×10^{-2} mol of methyltriphenylphosphonium bromide), under a nitrogen atmosphere, a solution of 1-(2-chloroethyl)-2-formylpyrrole (**4a**) (1.5 g, 9.5×10^{-3} mol) in anhydrous THF (30 mL) was added. The reaction mixture was stirred at room temperature for 7 h and then treated with a 50% aqueous solution of sodium hydroxide and extracted with ethyl ether. The combined organic extracts were washed with water, dried (Na_2SO_4), and evaporated in vacuo to give a residue which was distilled at reduced pressure to afford **6a** (0.512 g, 4.3×10^{-3} mol, 45% yield) as a yellow oil.

2-(1-Methylethenyl)-1-vinylpyrrole (6b). Using the same procedure employed for the methylenation described above but with **5b** (0.65 g, 4.8×10^{-3} mol) yielded, after distillation at reduced pressure, **6b** (0.255 g; 1.92×10^{-3} mol, 40% yield) as a colorless liquid: bp 40 °C, $P = 1 \times 10^{-3}$ mbar; ^{1}H NMR δ 7.05 (dd, 1H, J = 8.8, 15.7 Hz), 6.98 (m, 1H), 6.21−6.16 (m, 2H), 5.18 (m, 1H), 5.14 (dd, 1H, J = 1.3, 15.7 Hz), 4.91 (m, 1H), 4.71 (d, 1H, J = 8.8 Hz), 2.08 (m, 3H); m/z 133 (M^+, 98), 118 (100), 104 (55), 91(16.5), 77 (11). Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.30; H, 8.35; N, 10.45.

3-(1-Methylethenyl)-1-vinylpyrrole (10). Using the same procedure employed for the methylenation described above but with 3-acetyl-1-vinylpyrrole (**9**) (1.0 g, 7.4×10^{-3} mol) yielded, after distillation at reduced pressure, **10** (0.443 g; 3.3×10^{-3} mol, 45%yield) as a colorless oil: bp 40 °C, $P = 2 \times 10^{-3}$ mbar; ^{1}H NMR δ 6.89 (m, 1H), 6.82 (m, 1H), 6.76 (dd, 1H, J = 8.65, 15.50 Hz), 6.40 (m, 1H), 5.21 (m, 1H), 5.07 (dd, 1H, J = 1.46, 15.50 Hz), 4.82 (m, 1H), 4.62 (dd, 1H, J = 1.46, 8.70 Hz), 2.02 (m, 3H); m/z 133 (M^+, 100), 118 (68), 106 (9.5), 93 (33), 77 (14), 65 (27), 51 (25), 39 (42). Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.17; H, 8.32; N, 10.60.

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