Diels-Alder Reactions of 2- and 3-Vinyl-1-(phenylsulfonyl)pyrroles

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Regioselectively produced 2- and 3-acetyl-1-(phenylsulfonyl)pyrroles can be reduced to the corresponding alcohols and subsequently dehydrated to afford *N*-protected vinylpyrroles. These remarkably stable vinylpyrroles can then serve as heterodienes in [4 + 2] cycloaddition reactions with electron deficient dienophiles to afford tetrahydroindole derivatives.

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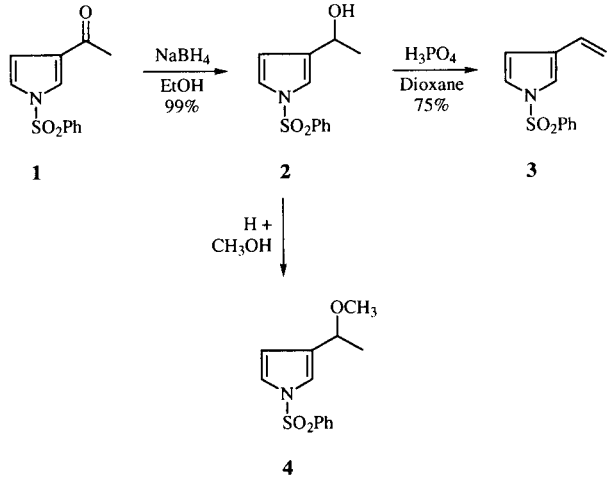
Vinyl pyrroles have been shown to act as heterocyclic dienes in [4 + 2] cycloaddition reactions with electron deficient alkenes or alkynes, and therefore represent valuable synthons to highly functionalized indole ring systems [1-7]. However, the potential of this methodology as a general route to annellated pyrroles has been somewhat limited by the high reactivity (*e.g.*, acid sensitivity) of the pyrrole nucleus as well as the inherent difficulty of preparing 3-substituted derivatives. In principle, both challenges are amenable to solution by the utilization of an arylsulfonyl protecting group for the pyrrole nitrogen, since the protecting group can serve to attenuate the normally high reactivity of this π-excessive heterocycle as well as site-direct substitution. Thus, while pyrroles typically undergo reaction with electrophiles predominantly at the C-2 (α) position [8], *N*-(phenylsulfonyl)pyrroles display a tunable reactivity in Friedel-Crafts acylations wherein the site of substitution is largely determined by the nature of the attacking electrophilic species [9,10]. In this manner then, a wide variety of 2- and 3-acyl-1-(phenylsulfonyl)pyrroles are readily accessible in high yield by the proper choice of Lewis acid catalyst.

For some time now, we have sought to exploit the unique reactivity imparted upon the pyrrole nucleus by virtue of the *N*-phenylsulfonyl protecting group and now wish to report that such regioselectively prepared acetyl derivatives can be efficiently reduced to the corresponding alcohols using sodium borohydride and subsequently dehydrated to afford 2- and 3-vinyl-1-(phenylsulfonyl)-pyrroles. These crystalline vinylpyrroles are remarkably robust (*vide infra*), and can serve as diene components in Diels-Alder reactions with certain electron deficient dienophiles to afford tetrahydroindole derivatives.

Recently, Salvadori *et al.* [11] employed such an acylation-reduction strategy to prepare a variety of 3-vinylpyrroles by a sequence involving initial regioselective C-3 acylation of 1-tosylpyrrole, reduction of the resultant ketones to the corresponding alcohols followed by dehydration under neutral conditons. Although our approach to the vinyl-1-(phenylsulfonyl)pyrrole precursors utilized in our Diels-Alder studies essentially parallels that of Salvadori, there are some dramatic differences in the reduction and dehydration sequences which are worthy of comment. For instance, although there are several methods available for the reductive deoxygenation of acyl-1-(phenylsulfonyl)pyrroles [12], the simple reduction of pyrrolyl ketones to the corresponding alcohols has not been thoroughly investigated. However, in an interesting finding of some generality, Muchowski observed that acylpyrroles can be reduced to the corresponding alky derivatives with sodium borohydride in boiling 2-propanol [13]; results in concert with an earlier observation of Dolby using sodium borohydride in refluxing dioxane [14].

In order to produce the alcohols required for their study, Salvadori *et al.* employed a modification (*e.g.*, sodium borohydride and 2-propanol in refluxing dioxane) of the Muchowski protocol for the reduction of 3-acyl-1-tosylpyrroles and along with the desired alcohols observed appreciable reductive deoxygenation of the ketones to the corresponding alkyl groups. In contrast to these results, we find that reduction of 3-acetyl-1-(phenylsulfonyl)pyrrole (**1**) can be cleanly effected to the alcohol level using sodium borohydride in ethanol (0° to rt). As no byproducts were observed (tlc) in this reduction step, the labile alcohol **2** was not further purified but used directly in the

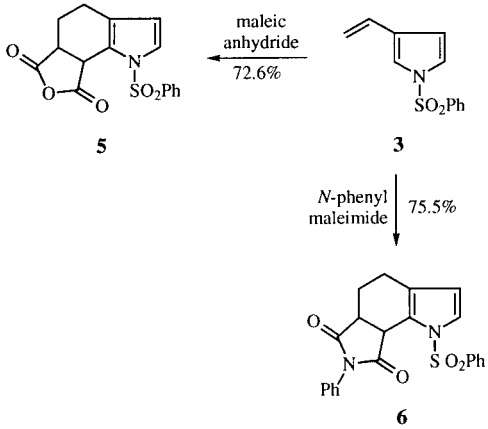
Scheme 1



subsequent dehydration step. Moreover, although the analogous *N*-tosyl alcohols were apparently susceptible to decomposition and were best dehydrated under neutral conditions (dimethyl sulfoxide, 160°) [11], we find that the alcohol **2** can be efficiently dehydrated using phosphoric acid in refluxing dioxane to afford the desired 3-vinyl species **3** in 75% overall yield. Interestingly, when this dehydration step was attempted in refluxing methanol, only the methyl ether **4** was obtained (Scheme 1).

Reaction of 3-vinyl-1-(phenylsulfonyl)pyrrole (**3**) with maleic anhydride in refluxing toluene (20 hours) afforded a 73% yield of the tetrahydroindole **5** (Scheme 2). Apparently the initial Diels-Alder adduct undergoes a spontaneous [1,3] sigmatropic hydrogen rearrangement to afford the rearomatized pyrrole product. Similar results were obtained upon reaction of **3** with *N*-phenylmaleimide which produced **6** in 75% yield (44 hours). In light of the prolonged reaction times required for cycloadditions with these dienophiles, it is perhaps not suprising that **3** was recovered unchanged after attempted reaction with the less reactive dienophiles ethyl acrylate or acrylonitrile under similar conditions for periods of 2-4 days.

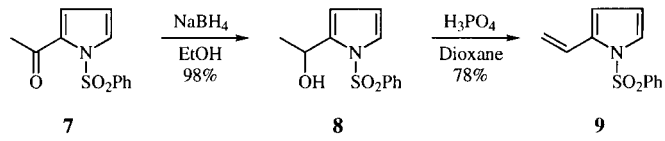
Scheme 2



Attempts to catalyze the latter cycloadditions of **3** were made using aluminum chloride (-78°, methylene chloride). However, use of this catalyst resulted in the formation of a putative cycloadduct (tlc) between two vinylpyrrole molecules, which upon attempted purification using column chromatography (silica gel) apparently underwent cycloreversion to afford the starting pyrrole.

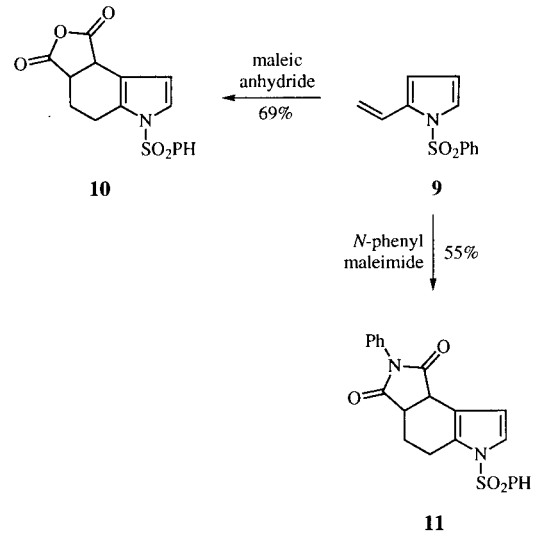
The synthesis and reactions of 2-vinyl-1-(phenylsulfonyl)pyrrole paralleled those of the 3-vinyl analogue. Thus, reduction of 2-acetyl-1-(phenylsulfonyl)pyrrole (**7**) with sodium borohydride (0° to rt) afforded the corresponding alcohol **8** which likewise was subjected to dehydration using phosphoric acid in refluxing dioxane to afford the 2-vinyl species **9** in 78% yield overall (Scheme 3).

Scheme 3



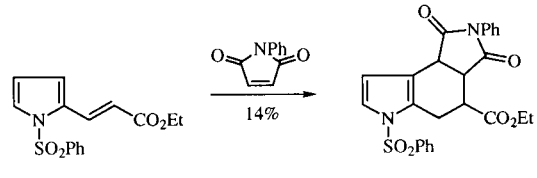
Reaction of 2-vinyl-1-(phenylsulfonyl)pyrrole (**9**) with maleic anhydride in refluxing toluene (18 hours) afforded a 69% yield of the tetrahydroindole **10**. Similar results were obtained upon reaction of **9** with *N*-phenylmaleimide, which produced **11** in 55% yield after 34 hours (Scheme 4).

Scheme 4



In order to elucidate the effects of substituents on the ease of Diels-Alder reactions of vinylpyrroles, the cycloaddition reaction of ethyl 3-[2-(1-phenylsulfonylpyrrolyl)]-3-propenoate (**12**) [15] with *N*-phenylmaleimide was conducted in refluxing toluene for 10 days. However, this reaction yielded only 14% of the Diels-Alder product **13** (Scheme 5) along with 30% of recovered starting material. Obviously, decreasing the electron density on the diene system significantly reduces its reactivity towards cycloaddition reactions.

Scheme 5



In conclusion, we find that vinyl-1-(phenylsulfonyl)-pyrroles can be easily prepared in high yields, display a remarkable stability towards weak acids and high temperatures, and can serve as efficient dienes in Diels-Alder reactions with reactive dienophiles. Moreover, as vinyl-1-(phenylsulfonyl)pyrroles represent useful synthons to highly functionalized indoles, the application of this methodology to the synthesis of indole alkaloids is currently under investigation.

EXPERIMENTAL

Melting points were determined in open capillaries with an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier transform (FT) instrument. The ^1H and ^{13}C nmr data were obtained on an IBM NR/100 FT NMR at 100 MHz in deuteriochloroform solution unless otherwise indicated. Chemical shifts are reported in δ (ppm) downfield from tetramethylsilane as an internal standard; coupling constants (J) are in Hertz (Hz). Mass spectra (CI) were obtained using a Finnigan INCOS 50 spectrometer. The following abbreviations are used to describe peak patterns where appropriate: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Flash column and thin layer chromatography were performed on silica gel with the indicated solvent systems.

General Procedure for the Reduction of Acetyl-1-(phenylsulfonyl)pyrroles Using Sodium Borohydride. Preparation of 1-[1-(Phenylsulfonyl)pyrrol-3-yl]ethanol (**2**).

To a solution of 3-acetyl-1-(phenylsulfonyl)pyrrole (0.5 g, 2.0 mmoles) in ethanol (15 ml) at 0° was added sodium borohydride (0.15 g, 4.0 mmoles) and the resulting mixture was stirred at room temperature for 2 hours. After this time, the mixture was quenched with water (10 ml) and the aqueous layer extracted with methylene chloride (3 x 20 ml). The combined organic extracts were washed with 10% aqueous sodium bicarbonate, water, and brine, dried (sodium sulfate), filtered and evaporated to give **2** as clear oil, 0.50 g (99%); ir: ν 3551, 2973, 1445, 1370, 1173, 1061, 879, 724 cm^{-1}; ^1H nmr: δ 1.45 (d, 3H, J = 6.7 Hz), 1.72 (s, 1H), 4.77 (m, 1H), 6.31 (dd, 1H, J = 1.7, 3.0 Hz), 7.13 (m, 2H), 7.45 (m, 3H), 7.85 (m, 2H); ^{13}C nmr: δ 24.0, 64.2, 112.0, 116.6, 121.4, 126.8, 129.4, 133.8, 134.2, 139.0.

Preparation of 1-[1-(Phenylsulfonyl)pyrrol-2-yl]ethanol (**8**).

Using the same procedure employed for the sodium borohydride reduction described above, but with 2-acetyl-1-(phenylsulfonyl)pyrrole (5.0 g, 20.0 mmoles) yielded **8** as a clear oil, 4.95 g (98%); ir: ν 3558, 2983, 1448, 1367, 1176, 1087, 731 cm^{-1}; ^1H nmr: δ 1.51 (d, 3H, J = 6.49 Hz), 3.04 (d, 1H, J = 4.15 Hz), 5.01 (dd, 1H, J = 4.15, 6.49 Hz), 6.27 (m, 2H), 7.29 (m, 1H), 7.54 (m, 3H), 7.77 (m, 2H); ^{13}C nmr: δ 21.0, 61.2, 111.7, 112.1, 126.5, 129.5, 133.9, 139.0, 139.1.

Preparation of 1-[1-(phenylsulfonyl)pyrrol-3-yl]-1-methoxyethane (**4**).

A mixture of 1-[1-(phenylsulfonyl)pyrrol-3-yl]ethanol (0.4 g, 1.6 mmoles) and phosphoric acid (0.80 g) in methanol (30 ml) was heated under reflux for 2 hours. The mixture was then allowed to cool, diluted with water and extracted with methylene chloride. The organic extracts were washed with 10% aqueous sodium bicarbonate, water, and brine, dried (sodium sulfate), filtered and evaporated to afford **4** as a clear oil, 0.42 g (99%): ir: ν 3130, 2978, 2805, 1580, 1369, 1174, 1120, 1060, 725 cm^{-1}; ^1H nmr: δ 1.37 (d, 3H, J = 6.5 Hz), 3.16 (s, 3H), 4.24 (q, 1H, J = 6.5 Hz), 6.29 (dd, 1H, J = 1.6, 3.2 Hz), 7.10 (m, 2H), 7.45-7.63 (m, 3H), 7.85 (m, 2H); ^{13}C nmr: δ 21.7, 55.8, 72.5, 112.3, 117.7, 121.4, 126.7, 129.3, 131.4, 133.3, 139.0.

Anal. Calcd. for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70; N, 5.28. Found: C, 59.00; H, 5.50; N, 5.30.

General Procedure for the Dehydration of 1-[1-(Phenylsulfonyl)-pyrrol]ethanols. Preparation of 3-Vinyl-1-(phenylsulfonyl)pyrrole (**3**).

To a solution of 1-[1-(phenylsulfonyl)pyrrol-3-yl]ethanol (0.5 g, 2.0 mmoles) in 1,4-dioxane (15 ml) was added phosphoric acid (0.5 g, 5.1 mmoles) in 1,4-dioxane (15 ml). The resulting mixture was refluxed at 120° for 12 hours, allowed to cool, diluted with water, and extracted with methylene chloride. The combined organic extracts were washed with 10% aqueous sodium bicarbonate, water, and brine, dried (sodium sulfate), filtered and evaporated to afford a brown oil. The residue was then subjected to flash chromatography (hexanes-methylene chloride, 3:1) to afford **3** as a clear oil which solidified on standing, 0.35 g (75%). Recrystallization from methanol afforded the analytical sample: mp 41-42°; ir: ν 3137, 1639, 1371, 1175, 1100, 1062, 728 cm^{-1}; ^1H nmr: δ 5.14 (dd, 1H, J = 1.1, 10.9 Hz), 5.41 (dd, 1H, J = 1.1, 17.6 Hz), 6.47 (m, 2H), 7.12 (m, 2H), 7.45-7.63 (m, 3H), 7.87 (m, 2H); ^{13}C nmr: δ 111.0, 113.5, 118.4, 121.7, 126.8, 128.0, 128.2, 129.4, 133.6, 138.9; ms: m/z 234 $(M+1)^+$.

Anal. Calcd. for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00. Found: C, 61.69; H, 4.63; N, 5.99.

Preparation of 2-Vinyl-1-(phenylsulfonyl)pyrrole (**9**).

Using the same procedure for dehydration as described above, but with 1-[1-(phenylsulfonyl)pyrrol-2-yl]ethanol yielded **9** after flash chromatography (hexanes-methylene chloride, 3:1) as a clear oil which solidified on standing, 0.36 g (78%). Recrystallization from toluene afford the analytical sample, mp 66-67.5°; ir: ν 3142, 1612, 1366, 1187, 1151, 725, 528 cm^{-1}; ^1H nmr: δ 5.14 (dd, 1H, J = 1.3, 11.2 Hz), 5.46 (dd, 1H, J = 1.3, 17.6 Hz), 6.24 (m, 1H), 6.42 (m, 1H), 7.08 (dd, 1H, J = 11.2, 17.6 Hz), 7.31 (m, 1H), 7.43-7.58 (m, 3H), 7.81 (m, 2H); ^{13}C nmr: δ 111.8, 112.4, 115.2, 123.2, 125.4, 126.8, 129.2, 133.8, 134.1, 139.0; ms: m/z 234 $(M+1)^+$.

Anal. Calcd. for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00. Found: C, 61.83; H, 4.80; N, 6.01.

General Procedure for the Diels-Alder Reaction of Vinyl-1-(phenylsulfonyl)pyrroles with Maleic Anhydride. Preparation of 4,5,6,7-Tetrahydro-1-(phenylsulfonyl)indole-6,7-dicarboxylic Anhydride (**5**).

To a solution of 3-vinyl-1-(phenylsulfonyl)pyrrole (0.97 g, 4.16 mmoles) in toluene (150 ml) was added a solution of maleic anhydride (0.45 g, 4.59 mmoles) in toluene (50 ml). The resulting mixture was refluxed at 120° for 82 hours. After removal of toluene under reduced pressure, the yellow residue was recrystallized from methylene chloride to afford **5** as colorless crystals, 1.0 g (73%), mp 88-90°; ir (potassium bromide): ν 3132, 1783, 1369, 1172, 924, 729 cm^{-1}; ^1H nmr: δ 2.10 (m, 2H),

2.53 (m, 2H), 3.45 (m, 1H), 5.00 (d, 1H, J = 8.7 Hz), 6.16 (d, 1H, J = 3.4 Hz), 7.20 (d, 1H, J = 3.4 Hz), 7.49-7.68 (m, 3H), 7.98 (m, 2H); ^{13}C nmr: δ 23.0, 23.9, 40.1, 41.6, 112.5, 120.2, 124.2, 126.0, 127.4, 129.2, 134.0, 139.2, 168.3, 172.1; ms: m/z 332 $(M+1)^+$.

Anal. Calcd. for $C_{16}H_{13}NO_5S$: C, 58.00; H, 3.95; N, 4.23. Found: C, 58.54; H, 4.02; N, 4.21.

Preparation of 4,5,6,7-Tetrahydro-1-phenylsulfonyl-4,5-dicarboxylic Anhydride (**10**).

Using the same procedure for the Diels-Alder reaction using maleic anhydride but with 2-vinyl-1-(phenylsulfonyl)pyrrole (0.50 g, 2.15 mmoles) yielded **10** as colorless crystals after recrystallization from methylene chloride, 0.49 g (69%), mp 165-167°; ir (potassium bromide): ν 3139, 1777, 1366, 1178, 1124, 912, 725, 592, 556 cm^{-1}; ^{1}H nmr: δ 1.94 (m, 1H), 2.35 (m, 1H), 2.61 (m, 1H), 2.99 (m, 1H), 3.47 (m, 1H), 4.12 (d, 1H, J = 8.5 Hz), 6.40 (d, 1H, J = 3.5 Hz), 7.28 (d, 1H, J = 3.5 Hz), 7.49-7.69 (m, 3H), 7.80 (m, 2H); ^{13}C nmr: δ 18.9, 20.9, 39.9, 40.3, 110.8, 114.6, 122.5, 126.8, 129.4, 129.7, 134.3, 138.6, 170.3, 172.1; ms: m/z 332 $(M+1)^+$.

Anal. Calcd. for $C_{16}H_{13}NO_5S$: C, 58.00; H, 3.95; N, 4.23. Found: C, 58.10; H, 4.01; N, 4.20.

General Procedure for the Diels-Alder Reaction of Vinyl-1-(phenylsulfonyl)pyrroles with *N*-Phenylmaleimide. Preparation of 6-Phenylsulfonyl-1,3-dioxo-2-phenyl-1,3,3a,4,5,8b-hexahydro-2*H*,6*H*-pyrrolo[3,4-*g*]indole (**6**).

To a solution of 3-vinyl-1-(phenylsulfonyl)pyrrole (0.95 g, 4.29 mmoles) in toluene (100 ml) was added a solution of *N*-phenylmaleimide (0.58 g, 5.58 mmoles) in toluene (50 ml). The resulting mixture was refluxed at 120° for 44 hours. After removal of toluene, the resulting brown residue was submitted to flash chromatography (methylene chloride) to afford **6** as a white solid 1.25 g (76%), mp 209-210.5°; ir (potassium bromide): ν 3113, 1712, 1365, 1173, 724, 590 cm^{-1}; ^{1}H nmr: δ 1.90-2.64 (m, 4H), 3.40 (m, 1H), 4.97 (d, 1H, J = 8.6 Hz), 6.14 (d, 1H, J = 3.3 Hz), 7.12 (d, 1H, J = 3.3 Hz), 7.22-7.59 (m, 8H), 8.07 (m, 2H); ^{13}C nmr: δ 21.0, 24.6, 39.4, 41.1, 112.6, 122.9, 123.7, 125.8, 126.5, 127.5, 128.5, 129.0, 129.1, 131.9, 133.7, 139.5, 173.4, 177.6; ms: m/z 407 $(M+1)^+$.

Anal. Calcd. for $C_{22}H_{18}N_2O_4S$: C, 65.01; H, 4.46; N, 6.89. Found: C, 65.16; H, 4.37; N, 6.91.

Preparation of 6-Phenylsulfonyl-1,3-dioxo-2-phenyl-1,3,3a,4,5,8b-hexahydro-2*H*,6*H*-pyrrolo[3,4-*e*]indole (**11**).

Using the same procedure for the Diels-Alder reaction with *N*-phenylmaleimide as above, but with 2-vinyl-1-(phenylsulfonyl)pyrrole (0.73 g, 3.1 mmoles) yielded the adduct **11**, 0.70 g (55%), mp 170-172°; ir (potassium bromide): ν 3145, 1708, 1498, 1376, 1173, 729, 687, 597 cm^{-1}; ^{1}H nmr: δ 2.01 (m, 1H), 2.37 (m, 1H), 2.66 (m, 1H), 2.90 (m, 1H), 3.32 (m, 1H), 3.96 (d, 1H, J = 8.1 Hz), 6.52 (d, 1H, J = 3.5 Hz), 7.09-7.75 (m, 9H), 7.78 (m, 2H); ^{13}C nmr: δ 19.5, 21.9, 39.5, 40.0, 111.7, 117.1, 122.2, 125.2, 126.2, 126.7, 128.2, 128.5, 129.0, 129.5, 129.5, 131.7, 133.9, 137.6, 138.9, 175.7, 177.2; ms: m/z 407 $(M+1)^+$.

Anal. Calcd. for $C_{22}H_{18}N_2O_4S$: C, 65.01; H, 4.46; N, 6.89. Found: C, 65.05; H, 4.39; N, 6.75.

Preparation of Ethyl 3-[2-(1-Phenylsulfonylpyrrolyl)]-3-propenoate (**12**) from 2-Formyl-1-(phenylsulfonyl)pyrrole [15].

To a solution of 2-formyl-1-(phenylsulfonyl)pyrrole [9c] (0.2 g, 0.873 mmole) in methylene chloride (15 ml) at room temperature was added a solution of carboethoxymethylene triphenylphosphorane (0.386 g, 1.05 mmoles) in methylene chloride (12 ml). The solution was stirred for 20 hours and washed with 1 *N* hydrochloric acid (2 x 15 ml), brine, dried (sodium sulfate), filtered and evaporated. The residue was chromatographed on a column of silica gel (ethyl acetate-hexanes, 1:4) to afford pure **12**, 0.21 g (80%), mp 85.5-87°; ir (potassium bromide): ν 3135, 3000, 1701, 1625, 1451, 1367, 1185, 1125, 723, 586 cm^{-1}; ^{1}H nmr: δ 1.4 (t, 3H), 4.3 (q, 2H), 6.12 (s, 1H), 6.4 (t, 2H), 6.8 (d, 1H), 7.4-8.4 (m, 6H); ms: m/z 305 (M^+), 266, 167, 148, 141, 136, 119, 77 (100).

Anal. Calcd. for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95; N, 4.59. Found: C, 59.00; H, 4.89; N, 4.58.

Preparation of Ethyl 6-Phenylsulfonyl-1,3-dioxo-2-phenyl-1,3,3a,4,5,8b-hexahydro-2*H*,6*H*-pyrrolo[3,4-*e*]indole-4-carboxylate (**13**).

Using the same procedure for Diels-Alder reaction of 3-vinyl-1-(phenylsulfonyl)pyrrole with *N*-phenylmaleimide, but with the acrylate **12** (0.5 g, 1.6 mmoles) for 10 days yielded the adduct **13**, 0.11 g (14%), mp 199-201.5°; ir: ν 1728, 1717, 1370, 1183, 729 cm^{-1}; ^{1}H nmr: δ 1.25 (t, 3H, J = 7.07 Hz), 2.99 (m, 2H), 3.35 (d, 1H, J = 12.7 Hz), 3.92-4.28 (m, 4H), 6.50 (d, 1H, J = 3.45), 7.06-7.82 (m, 11H); ^{13}C nmr: δ 14.0, 21.6, 38.7, 40.5, 41.6, 61.4, 111.2, 117.7, 122.8, 126.1, 126.8, 127.8, 128.5, 128.9, 129.6, 131.5, 134.0, 138.8, 171.1, 175.1, 175.2.

Anal. Calcd. for $C_{25}H_{22}N_2O_6S$: C, 62.75; H, 4.64; N, 5.86. Found: C, 62.75; H, 4.68; N, 5.80.

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