STABLE ANTIAROMATIC 1,4-DIAZAPENTALENES: SYNTHESIS AND OXIDATION REACTION OF 2-VINYL- AND 2,5-DIVINYL-1,4-DIHYDRO-PYRROLO[3,2-*b*]PYRROLE DERIVATIVES

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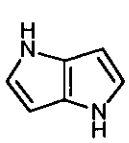
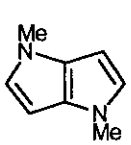
Abstract - Stable and isolable 8π electrons antiaromatic compounds, 2-vinyl and 2,5-divinyl substituted 1,4-diazapentalenes were synthesized *via* an oxidation reaction of correspondingly substituted 1,4-dihydro-3,6-di-*tert*-butylpyrrolo[3,2-*b*]pyrroles which were prepared by an electrophilic addtion reaction of dimethyl acetylenedicarboxylate (DMAD).

Recently occurred 10π electrons heterocyclic aromatic compound 1,4-dihydropyrrolo[3,2-*b*]pyrrole (**1**) has been interested in its extremely electron excess character compared to the familiar nitrogen heterocycles such as pyrrole and indole which have similar electronic structure. Therefore, the molecule would behave mainly as a very reactive compound towards electrophilic reagents. Although both unsubstituted molecule (**1**)[1] and *N,N'*-dimethyl derivative (**2**)[2] have been reported to be too labile to investigate the chemical behavior, 1,4-dihydro-3,6-di-*tert*-butylpyrrolo[3,2-*b*]pyrrole (**3**)[3] was found to be a fairly stable molecule. But, the electrophilic reaction of this molecule has not been explored extensively, except for Vilsmeier reaction and reaction with chlorosulfonyl isocyanate (CSI). The former gave 2-formyl derivative[4] and the latter gave 2,5-dicyano derivative.[5] In the process of studying the chemistry of 1,4-dihydropyrrolo[3,2-*b*]pyrrole system, we found out that the pyrrolo[3,2-*b*]pyrrole (**3**) gave dimethyl acetylenedicarboxylate (DMAD) adducts even at 0 °C. The present paper deals with the formation of 2-vinyl- and 2,5-divinyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives by an electrophilic addtion reaction of DMAD and the isolation of antiaromatic 3,6-di-*tert*-butylpyrrolo[3,2-*b*]pyrrole (1,4-diazapentalene) derivatives by an oxidation reaction of here obtained 1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives.



1



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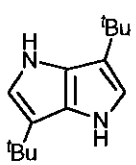

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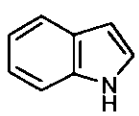
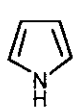


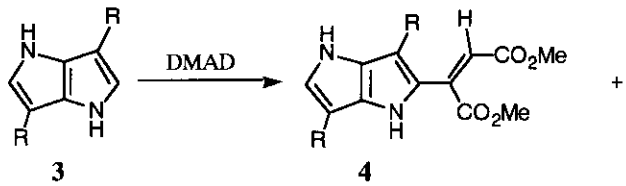
Indole



Pyrrole

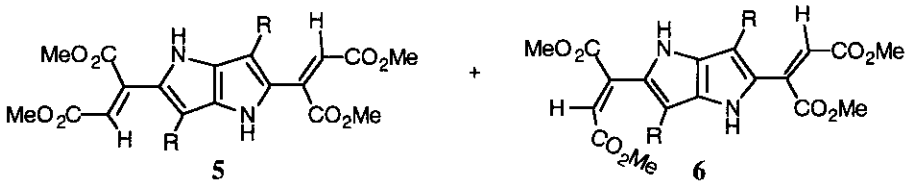
When a mixture of **3** and 1.3 equiv. of DMAD was stirred for 3 h at room temperature, an electrophilic reaction at the α-position of the nitrogen occurred to give 3,6-di-*tert*-butyl-2-(*cis*-1,2-dimethoxycarbonylvinyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**4**, mp 194 °C) in 31% yield together with two kind of divinyl compounds, 3,6-di-*tert*-butyl-2,7-bis(*cis*-1,2-dimethoxycarbonylvinyl)-1,4-dihydropyrrolo[3,2-

b]pyrrole (**5**, mp 204-205 °C) and 3,6-di-*tert*-butyl-2-(*cis*-1,2-dimethoxycarbonylvinyl)-7-(*trans*-1',2'-dimethoxycarbonylvinyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**6**, mp 152 °C) in 1% and 4% yields. Further reaction of **4** with excess of DMAD also gave 2,7-divinyl compounds (**5**) and (**6**). A stirred mixture of **4** and excess of DMAD at room temperature for 5 h gave **5** and **6** in 24% and 46% yields. The reaction suggests the extremely electron efficient character of **3**, because both pyrrole and indole did not give any adducts under the similar conditions.



3 **4**

R = ^{t}Bu



5 **6**

The structure determination of obtained adducts was carried out by inspection of ^{1}H and ^{13}C NMR data.[6-8] Compound (**5**) found to be a molecule having a C2 symmetry because of showing 11 signals (4 for Csp^3, 5 for Csp^2, and 2 for carbonyl) in ^{13}C NMR spectrum.[7] On the other hand, that of **6** showed 22 signals for respective carbon in the molecule (8 for Csp^3, 10 for Csp^2, and 4 for carbonyl) due to asymmetrical structure.[8] The ^{1}H NMR spectrum of **6** showed two vinyl-proton signals at δ 6.09 and 7.09, and two N-H signals at δ 7.41 and 7.74, both of which were found to be exchangeable with D_2O. The substituents effects on the chemical shifts for a vinyl-proton of trisubstituted ethylenes were well elucidated experimetally.[9] The δ_H value for the proton of mono-substituted maleate would be estimated as smaller than that of substituted fumalate by 0.6 - 1.0 ppm. The signals at δ 6.09 and 7.09 of **6** would be assigned to the maleate and fumalate moiety, respectively. Thus the structure of a symmetrical molecule (**5**) was confirmed as having a couple of maleate moieties, because a singlet signal of equivalent vinyl-protons observed at δ 6.13. Finally, the structure of **4** was confirmed from the observation of a coupling constant (J = 2.6 Hz) between N-H at δ 7.39 and ring proton at δ 6.60.[6] Further, the vinyl substituent of **4** was considered as maleate structure because of the obsevation of a signal at δ 6.10 which attributed to the substituent's proton.

A formation of labile antiaromatic 1,4-diazapentalene (**7**) from **3** with use of NiO_2 as an oxidizing agent has been reported.[10] Oxidation reaction of here obtained vinyl and divinyl compounds was also examined, respectively. When excess (100 mg, 1.1 mmol) of freshly prepared NiO_2[11] was added to an acetonitrile solution of **4** (30.6 mg, 0.085 mmol) and the resulted suspension was stirred for 20 min at room temperature. An oxidative dehydrogenation occurred to give 3,6-di-*tert*-butyl-2-(*cis*-1,2-dimethoxycarbonylvinyl)-1,4-diazapentalene (**8**, 26 mg, 85%, mp 33 - 35 °C) as a light brownish solid, after NiO_2 was removed by filtration using membrane filter and the filtrate was concentrated *in vaccuo*. The reaction could be monitored by a spectrophotometer using the supernatant solution of a heterogeneous

oxidation reaction mixture. Similar procedure for divinyl compounds (**5**) and (**6**) gave 1,4-diazapentalene (**9**) (mp 169 - 171 °C, 67%) and (**10**) (mp 36 - 38 °C, 80%), respectively. Thus obtained compounds did not show any spectral data which attributed to N-H both in ^{1}H NMR and in IR spectroscopy and found to be stable either in solid state or in solution under the atmospheric conditions. In the case of **5**, C2 symmetry was maintained during the oxidation reaction to give symmetrical 2,5-divinyl-1,4-diazapentalene (**9**) because four singlet signals and 11 signals (4 for Csp^3, 5 for Csp^2, and 2 for carbonyl) were observed in ^{1}H and ^{13}C NMR spectra, respectively.[12] The oxidized structure was also confirmed by a regeneration reaction giving dihydro compounds (**4**, **5** and **6**) from diazapentalenes (**8**, **9** and **10**) in the presence of dihydrobenzoquinone. A time-course electronic spectra (7 min intervals) of **8** in the presence of an equivalent of dihydrobenzoquinone (25 °C, in MeCN) was shown in Figure 1. Similar time dependent spectral change is also observed in **9** and **10**.

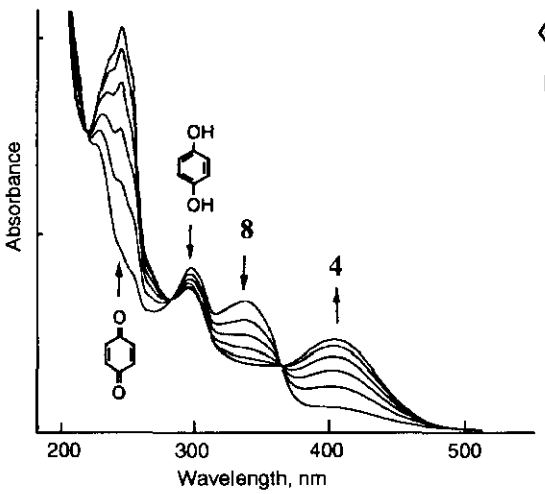
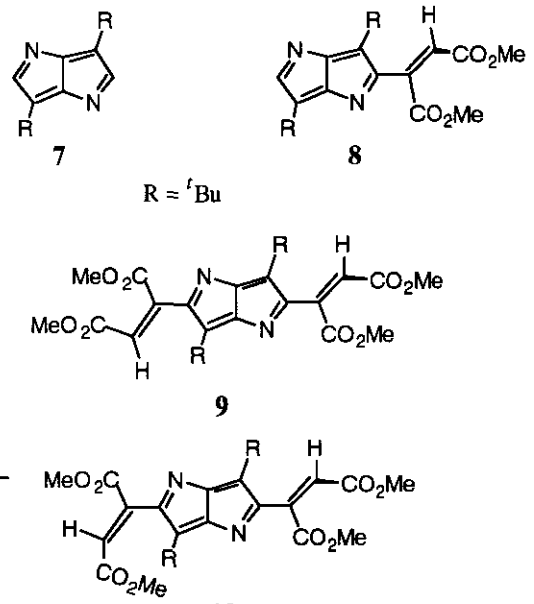


Figure 1. Observed spectral change during the reduction reaction of 1,4-diazapentalene (**8**) by hydroquinone in deaerated MeCN at 25 °C.



Paramagnetic schielding effect resulting from an antiaromatic planar 8π electron system on a ring-proton could be evaluated on the basis of ^{1}H NMR data of **8**. Diazapentalene (**8**) showed signals at δ 1.22 (s, 9H), 1.24 (s, 9H), 3.80 (s, 3H), 3.84 (s, 3H), 6.42 (s, 1H, vinyl proton), and 7.41 (s, 1H, ring-proton). Deviation between observed chemical shift of the ring-proton and estimated chemical shift value (δ 8.05 ppm) for conjugated five-membered ene-imine system[10] is calculated as Δδ = 0.64 ppm. The difference would be attributed to the paramagnetic shielding effect of diazapentalene (**8**), because the degree of shielding is comparative to ever reported antiaromatic compounds (**7**) (Δδ = 0.88 ppm)[10] and 1,4-dihydropyrazines[13] (Δδ ≈ 0.75 ppm).

ACKNOWLEDGEMENTS

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6. ^{1}H and ^{13}C NMR (200 and 50 MHz, $CDCl_3$) data for **4**: δ_H 1.32 (s, 9H), 1.41 (s, 9H), 3.78 (s, 3H), 3.89 (s, 3H), 6.10 (s, 1H), 6.60 (s, 1H, J = 2.6 Hz), 7.39 (br, 1H), and 7.74 (br, 1H); δ_C 30.6 (s), 30.9 (q), 31.7 (q), 32.3 (s), 51.9 (q), 52.8 (q), 118.0 (s), 118.5 (d), 118.9 (d), 119.3 (s), 122.8 (s), 127.9 (s), 129.2 (s), 142.7 (s), 165.7 (s), and 169.1 (s).
7. ^{1}H and ^{13}C NMR (200 and 50 MHz, $CDCl_3$) data for **5**: δ_H 1.44 (s, 18H), 3.79 (s, 6H), 3.86 (s, 6H), 6.13 (s, 2H), and 7.81 (br s, 2H); δ_C 31.7 (q), 32.2 (s), 52.0 (q), 52.9 (q), 117.7 (d), 121.5 (s), 125.0 (s), 129.4 (s), 141.8 (s), 165.3 (s), and 168.5 (s).
8. ^{1}H and ^{13}C NMR (200 and 50 MHz, $CDCl_3$) data for **6**: δ_H 1.26 (s, 9H), 1.47 (s, 9H), 3.66 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 3.88 (s, 3H), 6.09 (s, 1H), 7.09 (s, 1H), 7.41 (br s, 1H), and 7.74 (br s, 1H); δ_C 30.9 (q), 31.6 (q), 31.8 (s), 32.2 (s), 51.8 (q), 52.1 (q), 52.8 (q), 53.0 (q), 115.5 (s), 118.8 (s), 119.0 (d), 122.7 (s), 123.1 (s), 129.0 (s), 129.2 (s), 131.5 (d), 138.6 (s), 142.5 (s), 165.2 (s), 165.5 (s), 167.0 (s), and 168.9 (s).
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12. ^{1}H and ^{13}C NMR (200 and 50 MHz, $CDCl_3$) data for **10**: δ_H 1.23 (s, 18H), 3.80 (s, 6H), 3.84 (s, 6H), 6.41 (s, 2H); δ_C 29.9 (q), 33.5 (s), 52.4 (q), 52.8 (q), 129.6 (d), 139.2 (s), 148.1 (s), 162.1 (s), 164.2 (s), 165.0 (s), and 176.1 (s).
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