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NOTE

Reactivity of 2- and 4-Vinylpyrrole as Diene System towards Dienophiles

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IR and ^{1}H-NMR spectral data of 2- and 4-vinylpyrrole derivatives (**1**) and (**2**), respectively, indicate that the reactivity of compound (**1**) is higher than that of (**2**) towards dienophiles. Analysis of [4π + 2] cycloaddition reaction of vinylpyrrole derivatives (**1**) and (**2**) with dimethylacetylene-dicarboxylate (DMAD) has been studied to reflect the higher reactivity of compound (**2**).

Vinylfurans[1] and vinylthiophenes[2] have been shown to react with different dienophile systems; also many pyrrole derivatives have been reported to condense with dienophile systems such as maleic anhydride, benzoquinone and naphthoquinone to give indole derivatives[3]. 1-Substituted-2-and 3-vinylpyrrole have also been reported[3] to react with electron deficient dienophiles to form dihydro- and tetrahydroindols.

The reaction of 1-methyl-2-vinylpyrrole with acrylonitrile was reported to give 4-cyano-1-methyl-4,5,6,7-tetrahydroindole[4]. The reaction of dimethylacetylene-dicarboxylate (DMAD) with 1-methyl-2-vinylpyrrole is temperature dependent.

It has been shown that the reactivities of 2- and 3-vinylpyrrole are similar[4]. However, in our study, the reactivity of both 4-formyl-1-methyl-2-vinylpyrrole (**1**) and 2-formyl-1-methyl-4-vinylpyrrole (**2**) was studied to explore the reactivity of these compounds in view of factors like inductive and mesomeric effects.

IR spectra were obtained for nujol mulls using a Perkin–Elmer 577 spectrometer, between 4000 and 625 cm^{-1}. ^{1}H-NMR spectra were measured for *ca.* 0.3 M solution in $CDCl_3$ at 60 MHz using a JEOL JMN FX-100 spectrometer. All chemical shifts are reported relative to tetramethyl silane ($\delta = 0$) and the deuterated solvent was used as a lock signal for ^{1}H-NMR spectra.

General Reaction of the vinylpyrrole with DMAD:

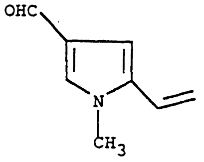
3-Formyl-5-vinyl-1-methylpyrrole (0.37 g, 0.003 mol) and hydroquinone (3 mg) in dry chloroform (15 mL) was added to dimethylacetylene-dicarboxylate (0.42 g), 0.003 mol) in chloroform (10 mL). The mixture was heated at 60°C under nitrogen for 3 days. The solvent was then removed under reduced pressure. The crude solid purified by recrystallization from toluene to give dimethyl-3-formyl-6,7-dihydro-1-methyl-indole-4,5-dicarboxylate (43%) had m.p. 145°C. (Found C, 60.70; H, 5.44; N, 5.10; requires C, 60.60; H, 5.54; N, 5.05%). IR ν_{max} (nujol) 1700, 1670 cm^{-1}; dH ($CDCl_3$) 2.70 (4H, br, s), 3.50 (3H, s), 3.70 (3H, s), 3.88 (3H, s), 7.10 (1H, s), 9.50 (1H, s).

2-Formyl-4-vinyl-1-methylpyrrole (0.37 g, 0.003 mol) and hydroquinone

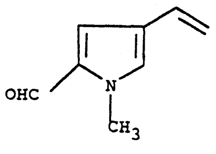
(3 mg) in dry chloroform (15 mL) was added to dimethylacetylene-dicarboxylate (0.42 g, 0.003 mol) in chloroform (10 mL). The mixture was heated at 60°C under nitrogen for 3 days; the solvent was then removed under reduced pressure. The crude solid was purified by recrystallization from toluene to give dimethyl-2-formyl-4,5-dilhydro-1-methyl indole-6,7-dicarboxylate (32%), m.p. 110–112°C. (Found C, 60.60; H, 4.43; N, 5.06; requires C, 60.60; H, 5.45; N, 5.05%). IR ν_{max} (nujol) 1710, 1670 cm^{-1}, dH ($CDCl_3$) 2.50 (4H, m), 3.60 (3H, s), 3.70 (3H, s) 3.80 (3H, s), 6.50 (1H, s); 9.30 (1H, s).

A study of IR spectrum of 2-vinylpyrrole derivative (**1**) indicates a stretching vibration at 1690 cm^{-1} $\nu(C{=}C)$ while the spectrum of (**2**) shows a peak for the stretching vibration of the $\nu(C{=}C)$ at 1675 cm^{-1}. This indicates that the 2-vinylpyrrole system (**1**) has more electron density which is more reactive towards the dienophile.

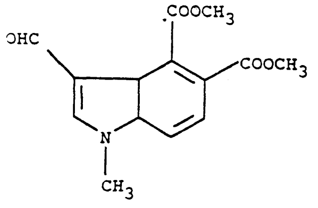
The ^{1}H-NMR data for both vinyl compounds presented in Table-1 shows different chemical shifts for both vinyl protons in compound (**1**), they appear downfield. This result may seem to contradict conclusions from the IR study since it suggests that (**2**) is more reactive than (**1**) towards dienophiles. This is not the case here, because the shift towards lower field in the NMR can be attributed to the nearby aromatic ring. This effect is less significant towards the reactivity of the vinyl system because it is well known that any substituent at position 2 in a 1,3 diene has less electronic influence upon the reactivity of the diene than does the corresponding substituent at position 1. However, electronwithdrawing formyl group at the 2-position of the 1-methyl-4-vinyl compound (**2**) deactivates the diene system because of the direct conjugation of the diene system in the 1-methyl-2-vinylpyrrole as shown in schemes 1 and 2. The (4π + 2) anticipated to give quantitative information on the reactivity of both vinyl groups gave indole derivative (**3**) with yield 43%, while that of 2-formyl-1-methyl-4-vinylpyrrole (**2**) gave 32% of product (**4**). It is, therefore, assured that the 2-vinyl compound (1) is more reactive than the 4-vinyl compound (**2**) towards dienophile and, thus, the electronic effects of the substituents of the 2-position have a significant influence on the activity of the diene system.



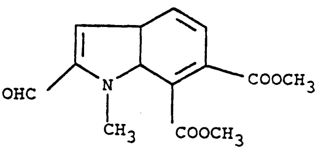
(1)



(2)

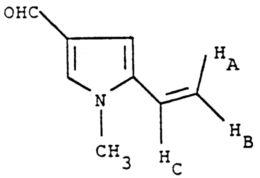
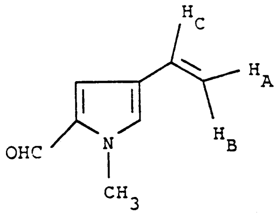


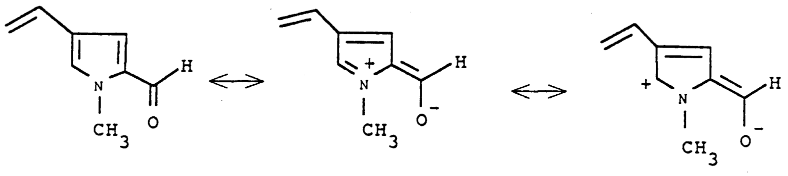
(3)



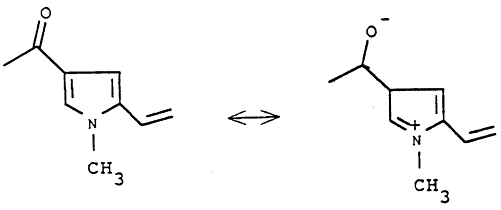
(4)

TABLE-1
^{1}H-NMR CHEMICAL SHIFTS OF COMPOUNDS (1) AND (2)

	H_A	H_B	H_B
 (1)	5.15	5.55	6.55
 (2)	4.90	5.35	6.42



Scheme 1



Scheme 2

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