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THE REACTIONS OF 1-METHYLPYRROLE AND 1-PHENYLPYRROLE WITH 3,4,5,6-TETRACHLORO-1,2-BENZOQUINONE AND 1,2-NAPHTHOQUINONE

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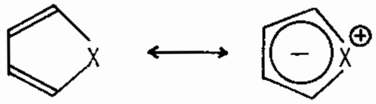
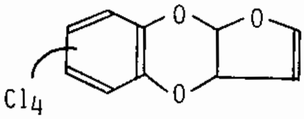
Abstract – The reactions of pyrrole derivatives with 3,4,5,6-tetrachloro-1,2-benzoquinone and 1,2-naphthoquinone afforded the keto-enol-type and the hydroquinone-type substitution products, respectively, via the nucleophilic attack of the pyrrole derivatives on the o-quinone derivatives.

Certain kinds of heterocyclic compounds are known to have aromaticity. Pyrrole (1; X=NR) and furan (1; X=O) derivatives belong to this class of heterocyclic aromatic compounds due to the contribution of the canonical formula (1a), which possesses the negative charge on the ring and the positive charge on the hetero-atom *in order to construct the 6 π-electron aromatic structure.*[1] On the other hand, azepine derivatives (2) have no aromaticity and generally behave as olefinic compounds.[2]

Recently, the reactions of heterocyclic compounds with conjugated olefins have attracted the attention of chemists from the view-point of their synthetic utility and the elucidation of the electronic nature of heterocyclic compounds. It has been published that furan reacts with 3,4,5,6-tetrachloro-1,2-benzoquinone (7) to afford the [4+2]-type cycloaddition product (3).[3] The authors have also documented that 7 reacts with azepine derivatives to give mainly the [4+2]- (4) and the [4+6]-type (5) cycloadducts.[4] As a part of our research on the reactivity of heterocyclic compounds,[4,5] we have studied the reactions of pyrrole derivatives with o-quinone derivatives in an effort to show that the difference in reactivity between pyrrole and azepine derivatives with o-quinone derivatives may be explained by differences in aromaticity. Here we wish to report on the result.



1 1a



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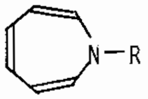

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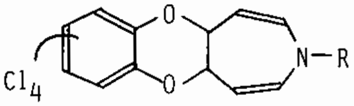

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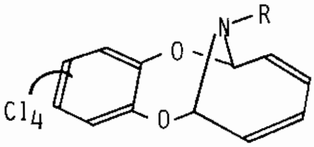

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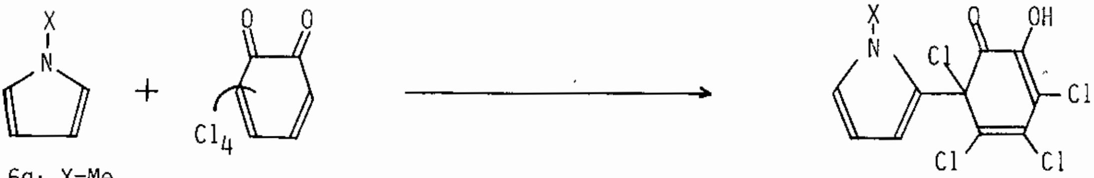
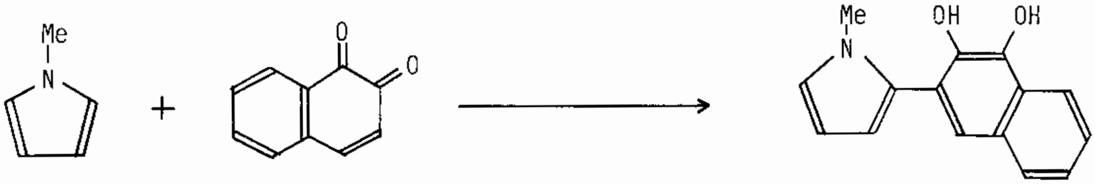


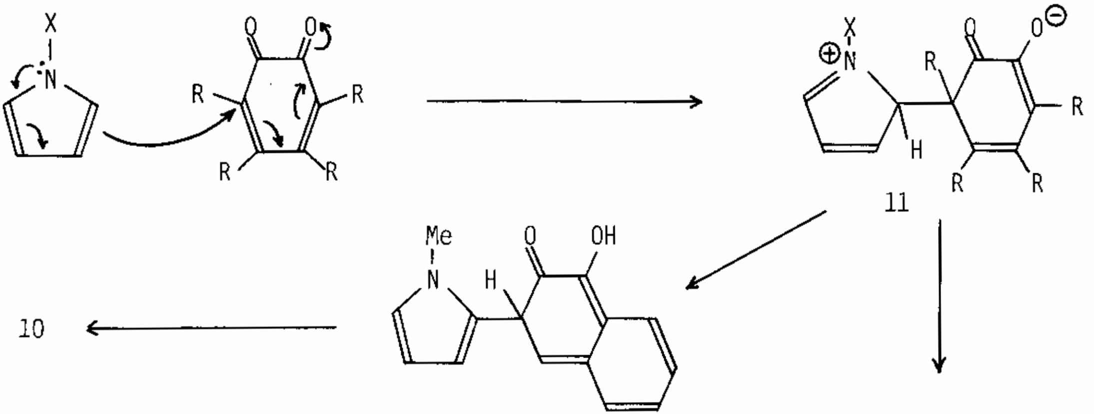
6a: X=Me
b: X=Ph

7

8a: X=Me
b: X=Ph



6a 9 10



11

12

8

1-Methylpyrrole (6a) and one molar equivalent of 7 were stirred in benzene at room temperature for 3 h. Silica gel chromatographic purification of the reaction mixture gave yellow crystals of a keto-enol-type substitution product (8a) in a 25% yield. Under analogous conditions, 1-phenylpyrrole (6b) was allowed to react with 7 for 18 h to give yellow crystals of 8b in a 14% yield. Reaction of 6a with one molar equivalent of 1,2-naphthoquinone (9) in benzene at room temperature for 2 weeks afforded colorless crystals of a hydroquinone-type substitution product (10) in a 5% yield. The reaction between 6b and 9 resulted in a quantitative recovery of 6b after stirring at room temperature for 5 weeks, and the reaction at 80°C for 3 days resulted in the recovery of 6b (48%) and unidentifiable resinous materials. *The physical properties of the products are as follows.*

8a: mp 122-123°C. Mass m/z (rel intens): 327 (M^+, 50), 292 (32), 108 (100). IR (KBr): 3400, 3030, 2950, 1697 cm^{-1}. UV (EtOH): 340 nm (log ε, 3.92). NMR ($CDCl_3$) δ ppm: 3.74 (s, 3H), 3.96 (bs, 1H), 6.02 (m, 1H), 6.06 (m, 1H), 6.61 (m, 1H).

8b: mp 151-152°C. Mass m/z (rel intens): 389 (M^+, 10), 170 (100), 115 (12). IR (KBr): 3440, 3030, 1683, 1598 cm^{-1}. UV (EtOH); 345 nm (log ε, 3.60). NMR ($CDCl_3$) δ ppm: 3.60 (bs, 1H), 6.24 (m, 1H), 6.64 (m, 1H), 6.72 (m, 1H), 7.1-7.5 (m, 5H).

10: mp 89-90°C. Mass m/z (rel intens): 224 (M^+-CH_3, 100), 179 (35), 117 (27). IR (KBr): 3440 (sharp), 3050, 2950, 1570 cm^{-1}. UV (EtOH): 268 nm (log ε, 4.19). NMR ($CDCl_3$) δ ppm: 3.53 (s, 3H), 6.34 (m, 2H), 6.40 (bs, 1H), 6.84 (bs, 1H), 7.30 (m, 1H), 7.4-8.3 (m, 5H).

The substitution pattern of the pyrrole ring moieties of the products was deduced on the basis of comparison of their NMR spectra to those of analogous compounds.[6] The keto-enol-form of 8 was indicated by its IR spectrum showing the absorption peaks due to the hydroxyl groups (3400 and 3440 cm^{-1}) and the carbonyl groups (1697 and 1683 cm^{-1}).

The reactions are thought to be a nucleophilic attack of the pyrrole derivatives on the o-quinone derivatives to give intermediate 11. The subsequent proton migration *in 11 affords the keto-enol-type product 8 and/or* the keto-enol-type intermediate 12, which then yields the hydroquinone-type product 10 via the enolization of the carbonyl group.

As mentioned above, the mode of the reaction of pyrrole derivatives with 7 are clearly different from those of furan and azepine derivatives. Pyrroles undergo a nucleophilic substitution reaction with 7 while furan and azepines afford the cycloaddition products in the reaction with 7.[3,4] This difference is considered to be attributable to the difference in the degree of the aromaticity of these heterocyclic compounds. It is well known that aromatic compounds undergo substitution reactions, but rarely undergo addition reactions. Azepines have no aromaticity and undergo cycloaddition reactions with olefinic compounds such as 7. Pyrroles are considered to have more aromatic character than furans because the oxygen atom in furans is more electro-negative than the nitrogen atom in pyrroles. This results in less negative charge residing on the ring of furen than pyrroles.[1] For this reason, pyrroles are believed to undergo substitution reactions with o-quinone derivatives and behave as aromatic heterocyclic compounds. On the other hand, furan which is less aromatic than pyrrole, affords the cycloaddition products and behave as a conjugated olefin.

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