Reaction of 2,4-Dinitrobenzenediazonium ions with Thiophens. Unprecedented Coupling to Electron-rich Methyl Groups

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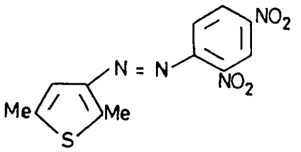
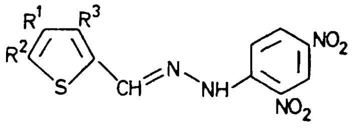
Summary 2,4-Dinitrobenzenediazonium ions couple normally with 2-t-butylthiophen to give the 5-azo-dye, but with 2,3,5-trimethylthiophen and tetramethylthiophen coupling occurs through methyl groups to give the corresponding 2,4-dinitrophenylhydrazones; 2,5-dimethylthiophen gives both the 3-azo-dye and the 2,4-dinitrophenylhydrazone of 5-methylthiophen-2-aldehyde.

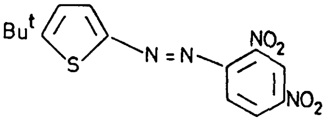
The coupling of reactive diazonium salts with acidic (electron deficient) methyl or methylene groups is well known.[1] Although the methyl group in 2,4-dinitrotoluene does not couple with 2,4-dinitrobenzenediazonium ions,[2] it is reported that the methyl group in 2,4,6-trinitrotoluene will couple with *p*-nitrobenzenediazonium ions.[3] However the coupling of diazonium salts with methyl groups in electron-rich sites, in an acidic medium, is we believe without precedent. The previous communication has reported how thiophen, both methylthiophens and thianaphthen are arylated when treated with 2,4-dinitrobenzene diazonium ions. In contrast 2-methyl- and 3-methyl-thianaphthenes and t-butylthiophen couple to yield azo-dyes. 2,5-Dimethylthiophen also couples in the 3-position to yield compound (**1**) (m.p. 137°) but in addition coupling through the methyl group occurs to yield the compound (**2**) (m.p. 233°) (identical with compound prepared from 2,4-dinitrophenylhydrazine and the aldehyde, m.p. mixed m.p., analysis, i.r. and n.m.r. spectra). 2-t-Butylthiophen couples to give compound (**3**) (m.p. 137°) as the major product. 2,3,5-Trimethylthiophen and tetramethylthiophen also couple with the diazonium ions, but in these cases the coupling is exclusively through the methyl group to yield the corresponding aldehyde phenylhydrazones (**4**) (m.p. 254°) and (**5**) (m.p. 247°) respectively. The methyl group in 2,3,5-trimethylthiophen which couples is not in the 2-position, and it is therefore assumed that it is the methyl group in the 5-position which is involved.



(1)



(2) $R^1 = H, R^2 = Me, R^3 = H$
(4) $R^1 = Me, R^2 = Me, R^3 = H$
(5) $R^1 = Me, R^2 = Me, R^3 = Me$



(3)

Bordwell and his co-workers treated 2,3-dimethylthianaphthen with acetyl nitrate in acetic acid–anhydride medium and obtained among other products 2-nitromethyl-3-methylthianaphthen.[4] Similar electrophilic attack on methyl group attached to aromatic nuclei has been observed in hexa-alkylbenzenes[5] and polyalkylnaphthalenes.[6] The remarkable feature about the present results is not only electrophilic substitution occurring on the methyl group, but that this reaction is taking place even when extremely reactive sites are vacant on the aromatic nucleus (*viz* 2,5-dimethylthiophen).

Analyses and spectra are consistent with the proposed structures.

(*Received*, 10*th December* 1973; *Com.* 1669.)

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