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ALKYLATION ORIENTATION RULES IN CONJUGATE ADDITION OF GRIGNARD REAGENTS TO NITROPYRROLE AND NITROTHIOPHENE SYSTEMS

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Conjugate addition of various Grignard reagents to 1-alkyl-2-nitropyrroles and to 2-nitrothiophene has been investigated. 1-Alkyl-2-nitropyrroles undergo alkylation at 3 and 5 positions with prevalence of the latter isomer. On the contrary, in 2-nitrothiophene system, formation of the 3-isomer prevails. In both systems, a bulkier Grignard reagent favours the 5-isomer formation. This trend can be reversed increasing steric hindrance exerted by the 1-substituent of 2-nitropyrrole. 1-(Tri-isopropylsilyl)-3-nitropyrrole and 3-nitrothiophene give exclusively the 2-isomer. This rection allows 2-alkyl-3-nitrothiophenes and pyrroles to be synthesized with a one-pot procedure instead of the classical multi-stage reaction.

Conjugate addition of alkyl Grignard reagents to nitroarenes[1] represents one of the most profitable procedures to accomplish alkylation of aromatic systems which do not enter the Friedel-Crafts reaction. This synthetic strategy is based on an irreversible attack of carbanions to the aromatic nucleus followed by oxidation of nitronate adduct intermediates to final products by addition of an external oxidizing agent. Owing to the irreversible formation of the intermediate, this reaction always follows fixed orientation rules, which reflect the relative reactivity of the various positions of the aromatic ring.

In other methods in which carbanions give a reversible attack to the nitroarenic systems such as the 'vicarious' substitution of hydrogen,[2] the alkylation orientation often depends on the nature of the substrate[3] and on the reaction conditions.[4] Moreover in these methods, a good leaving group must be placed on the carbanion to shift the reaction towards final products, thus increasing its steric hindrance. Hence, the relative reactivity of the various positions could be overturned.[3] For example, in nitrobenzene system the *ortho* and *para* positions should have a comparable reactivity as demonstrated by the reaction with methylmagnesium chloride,[5] while in 'vicarious' substitution *para* isomer is exclusively obtained in the case of the hindered α-chloroalkylphenylsulphones.[3]

In conclusion the addition of Grignard reagents represents the most correct approach to establish the relative reactivity of the various positions towards carbanion nucleophiles.

Although this reaction was applied to a large variety of aromatic systems,[5-7] no studies on pentaatomic heterocycles were yet reported notwithstanding the importance of these systems in organic chemistry. We wish to fill this gap reporting the results obtained with pyrrole and thiophene derivatives.

1-Substituted-2-nitropyrroles smoothly react with Grignard reagents to give both the 1,4 and the 1,6 addition products (compounds 3 and 4 respectively, scheme 1). The usual treatment with DDQ[8] allows one to isolate a mixture of 1-substituted-5-alkyl-2-nitropyrroles (5) and 1-substituted-3-alkyl-2-nitropyrroles (6) in good yields. 2-Nitrothiophene reacts likewise, while the reaction with 2-nitrofuran leads to an intractable mixture very likely due to the formation of ring-opened compounds. Separation of isomers 5 and 6 is very difficult. Nevertheless the characterization of compounds 5 and 6 and the determination of their ratio can easily be performed by ^{1}H-NMR analyses of the two isomers mixture (see experimental). As shown in table 1, the 5-alkyl substituted isomer prevails in pyrrole system, *vice versa* in thiophene system the 3-alkyl substituted compound predominates.

The isomer ratio is affected by steric factors. In thiophene system an increase of isomer 6 amount is observed with the increase in the bulkiness of the alkyl group, due to the steric hindrance exerted by the nitronate function on the 3-position. In 1-methylpyrroles, this trend is much less pronounced, because the steric influence of the nitro group on the 3-position is balanced by an analogous effect of the 1-methyl substituent on the 5-position. In fact with the bulkier 1-benzylpyrroles, the tendency is quite reversed.

Reaction on pyrroles requires protection of the N-H acidic hydrogen, since the corresponding nitropyrrole anions do not enter the reaction. Due to its ease of removal on aqueous work up, the trimethylsilyl group seems to be the most suitable protective function. Unfortunately, while the formation of 1-trimethylsilylpyrrole is a very simple procedure, the silylation of the corresponding nitro derivatives failed under the same experimental conditions.

The reaction of alkyl Grignard reagents with 1-(tri-isopropylsilyl)-3-nitropyrrole (7a) and 3-nitrothiophene (7b) followed by the usual treatment with DDQ[8] led exclusively to the 2-alkylated isomer (Scheme 2). In these cases, in contrast to the reaction with 2-nitroderivatives, yields are larger in

SCHEME 1

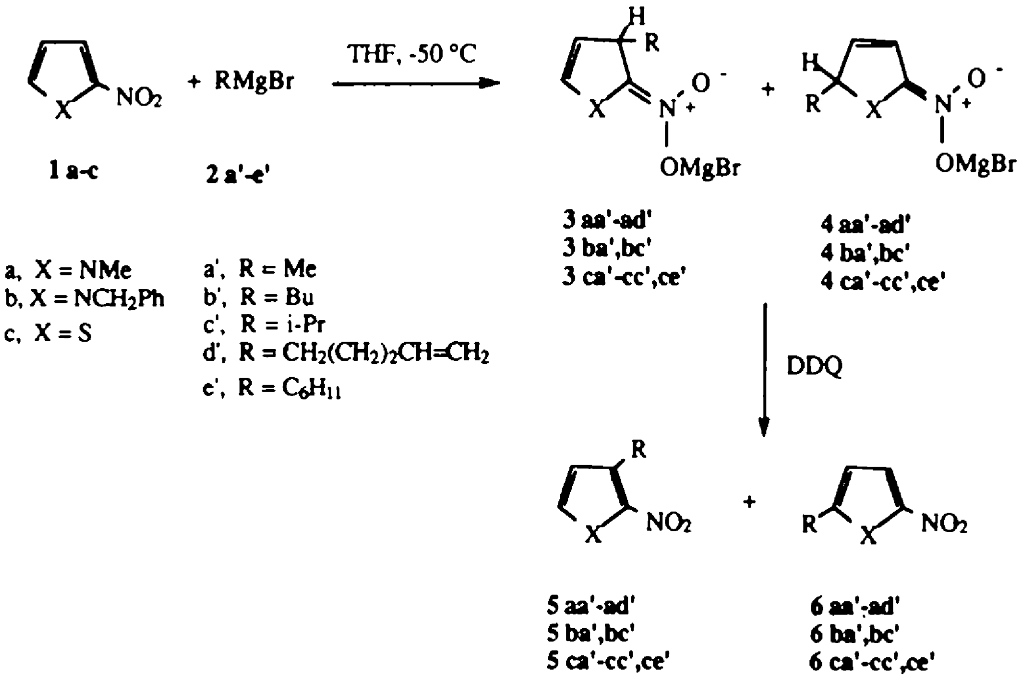
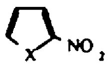


Table 1 - Conjugate Addition of Alkyl Grignard Reagents to 2-Nitrothiophenes and 1-Alkyl-2-nitro-pyrroles in THF at -50 °C.

Substrate 		R in RMgBr		Global yields (%)	Isomer ratio 5:6
X = NMe	(**1a**)	Me	(**2a'**)	72 (**5 aa'** + **6 aa'**)	40 : 60
X = NMe	(**1a**)	Bu	(**2b'**)	54 (**5 ab'** + **6 ab'**)	33 : 67
X = NMe	(**1a**)	i-Pr	(**2c'**)	61 (**5 ac'** + **6 ac'**)	30 : 70
X = NMe	(**1a**)	$CH_2(CH_2)_2CH{=}CH_2$	(**2d'**)	57 (**5 ad'** + **6 ad'**)	30 : 70
X = NCH_2Ph	(**1b**)	Me	(**2a'**)	67 (**5 ba'** + **6 ba'**)	35 : 65
X = NCH_2Ph	(**1b**)	i-Pr	(**2c'**)	74 (**5 bc'** + **6 bc'**)	48 : 52
X = S	(**1c**)	Me	(**2a'**)	67 (**5 ca'** + **6 ca'**)	87 : 13
X = S	(**1c**)	Bu	(**2b'**)	55 (**5 cb'** + **6 cb'**)	83 : 17
X = S	(**1c**)	i-Pr	(**2c'**)	52 (**5 cc'** + **6 cc'**)	78 : 22
X = S	(**1c**)	C_6H_{11}	(**2e'**)	52 (**5 ce'** + **6 ce'**)	64 : 36

thiophene than in pyrrole system. Generally, it was found that, when the substrate presents only one reactive position, steric effects enhance the side-reactions (redox products).[9] As a consequence, the lower yields in the case of **9 aa'-ac'** can easily be attributed to the steric hindrance exerted by the bulky tri-isopropylsilyl group on the 2-position.

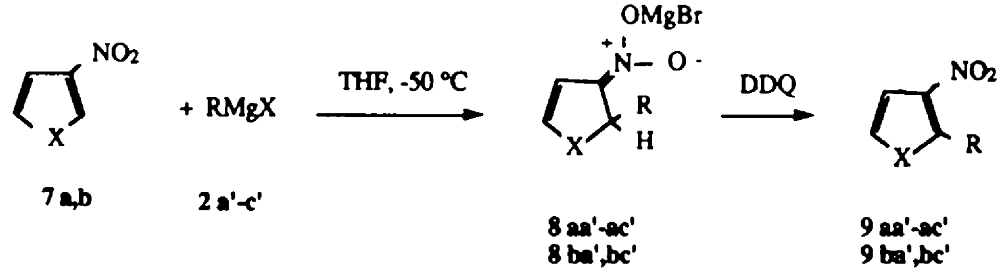
2-Alkyl-5-nitro and 3-alkyl-2-nitrothiophenes can be easily prepared by nitration of the corresponding alkyl thiophenes, since they are the predominant isomers obtained in these reactions. For example, nitration of 2-methylthiophene gives the 5- and the 3-nitro derivatives from 7:3[10] to 4:1[11] ratio, whereas the same reaction on 3-methylthiophene leads to a mixture of 2- and 5-nitro isomers in about 4:1[12] ratio. Therefore the conjugate addition of RMgX to 2-nitrothiophene can compete with direct nitration for the preparation of 3-alkyl-2-nitrothiophenes, if the 3-alkylthiophenes are difficultly available. On the other hand, conjugate addition is an exclusive one-pot method for the synthesis of 2-alkyl-3-nitrothiophenes. In fact, these compounds are obtained as the minor isomer by direct nitration of 2-alkylthiophenes; alternatively the synthesis requires a multi-stage reaction starting from the corresponding 2-alkyl-5-methoxycarbonyl derivative *via* nitration and decarboxylation.[13] Analogous considerations can be made for pyrrole system.[14]

In conclusion the conjugate addition of Grignard reagents to π-excessive heterocycles occurs smoothly in pyrrole and thiophene systems, while it fails in furan system. Furthermore, this reaction allows for the facile synthesis of the less readily available 2-alkyl-3-nitrothiophenes or pyrroles.

EXPERIMENTAL

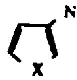
^{1}H-NMR spectra were recorded with a Varian EM390L instrument. Chemical shifts are given in p.p.m. from Me_4Si in $CDCl_3$ solutions. IR spectra were recorded with a Perkin-Elmer 257 spectrometer. VPC Analyses were performed on a Carlo Erba Fractovap 4160 HRGC instrument using OV1 capillary column. Melting points are uncorrected and were determined with a Buchi apparatus. THF was dried by refluxing it over sodium wire until the blue colour of benzophenone ketyl persisted and then

SCHEME 2



a, X = NSi(i-Pr)$_3$ a', R = Me
b, X = S b', R = Bu
c', R = i-Pr

Table 2- Conjugate Addition of Alkyl Grignard Reagents to 3-Nitrothiophenes and 3-Nitro-1-(triisopropylsilyl)pyrroles in THF at -50 °C.

Substrate 	R in RMgBr		Yields (%)
X = NSi(i-Pr)$_3$ (**7a**)	Me	(**2a'**)	62 (**9 aa'**)
X = NSi(i-Pr)$_3$ (**7a**)	Bu	(**2b'**)	58 (**9 ab'**)
X = NSi(i-Pr)$_3$ (**7a**)	i-Pr	(**2c'**)	51 (**9 ac'**)
X = S (**7b**)	Me	(**2a'**)	70 (**9 ba'**)
X = S (**7b**)	i-Pr	(**2c'**)	74 (**9 bc'**)

distilling it into a dry receiver under nitrogen atmosphere. Grignard reagents were titred before use.[15] 2-Nitrothiophene was obtained in more than 99% isomeric purity by treatment with chlorosulphonic acid of the commercial product.[16]

2-Nitropyrrole,[17] 1-tri-isopropylsilyl-3-nitropyrrole[18] and 3-nitrothiophene[19] were prepared by nitration of the corresponding heterocycle according to the literature.

2-Nitro-1-benzyl and 2-nitro-1-methylpyrroles were prepared from the corresponding nitro derivative in 90% and 82%, respectively, by reaction with sodium hydride (2:1 molar ratio) and alkyl halide (2:1 molar ratio) in THF at room temperature for 30 minutes.

Preparation of Alkylnitroheterocycles from the Corresponding Nitroarenes. General Procedure.

A 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and a dropping funnel was charged under nitrogen atmosphere with the appropriate nitro compound (5 mmol) in dry THF (20 mL). The solution was cooled at -50 °C and the Grignard reagent (5.5 mmol) was added dropwise. After about 15 minutes a THF solution of 6 mmol of DDQ was added to the stirred reaction mixture and stirring was continued for three hours. The mixture was quenched with saturated aqueous ammonium chloride, extracted with ether, dried with Na$_2$SO$_4$, evaporated under reduced pressure and purified by chromatography on a silica gel column eluting with cyclohexane : ethyl acetate (4 :1). Pure compounds were recovered from 3-nitroheterocycles. The mixture of two isomers obtained in the case of products arising from 2-nitroheterocycles, isolated as thick oil, was not submitted to more sophisticated chromatographic separation methods[20] required for the isolation of the pure compounds.

1,3-dimethyl-2-nitropyrrole (**5 aa'**): ^{1}H-NMR (CDCl$_3$) δ 2.44 (s,3H, CMe); 3.95 (s, 3H, NMe); 6.05 (d, 1H, H-4, $J_{4,5}$ = 2.88 Hz); 6.71 (d, 1H, H-5);IR (film); ν 1540 and 1350 (NO$_2$) cm^{-1}.

1,5-dimethyl-2-nitropyrrole (**6 aa'**): ^{1}H-NMR (CDCl$_3$) δ 2.31 (s,3H, CMe); 3.87 (s, 3H, NMe); 6.01 (d, 1H, H-4, $J_{4,3}$ = 4.50 Hz); 7.17 (d, 1H, H-3); ν 1540 and 1350 (NO$_2$) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 51.40; H, 5.70; N, 20.00% (C$_6$H$_8$N$_2$O$_2$ requires C, 51.43; H, 5.71; N, 20.00%).

3-butyl-1-methyl-2-nitropyrrole (**5 ab'**): ^{1}H-NMR (CDCl$_3$) δ 1.01 (t, 3H, CH$_3$, J=7.50 Hz); 1.66-1.86 (m, 4H, CH$_2$CH$_2$); 3.43 (t, 2H, CH$_2$, J=9.00 Hz); 3.94 (s, 3H, NMe); 6.10 (d, 1H, H-4, $J_{4,5}$ = 2.88 Hz); 6.73 (d, 1H, H-5); ν 1540 and 1350 (NO$_2$) cm^{-1}.

5-butyl-1-methyl-2-nitropyrrole (6 ab'): ^{1}H-NMR ($CDCl_3$) δ 0.96 (t, 3H, CH_3, J=7.50 Hz); 1.43-1.66 (m, 4H, CH_2CH_2); 2.62 (t, 2H, CH_2, J=9.00 Hz); 3.87 (s, 3H, NMe); 6.01 (d, 1H, H-4, $J_{4,3}$ = 4.45 Hz); 7.19 (d, 1H, H-3); ν 1540 and 1350 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 59.30; H, 7.70; N, 15.40% ($C_9H_{14}N_2O_2$ requires C, 59.34; H, 7.69; N, 15.38%).

1-methyl-2-nitro-3-isopropylpyrrole (5 ac'): ^{1}H-NMR ($CDCl_3$) δ 1.23 (d, 6H, CH_3, J=6.81 Hz); 3.58 (m, 1H, CH); 3.95 (s, 3H, NMe); 6.12 (d, 1H, H-4, $J_{4,5}$ = 2.88 Hz); 6.71 (d, 1H, H-5); ν 1540 and 1350 (NO_2) cm^{-1}.

1-methyl-2-nitro-5-isopropylpyrrole (6 ac'): ^{1}H-NMR ($CDCl_3$) δ 1.29 (d, 6H, CH_3, J=6.83 Hz); 2.95 (m, 1H, CH); 3.91 (s, 3H, NMe); 6.03 (d, 1H, H-4, $J_{4,3}$ = 4.45 Hz); 7.21 (d, 1H, H-3); ν 1540 and 1350 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 57.10; H, 7.15; N, 16.70% ($C_8H_{12}N_2O_2$ requires C, 57.14; H, 7.14; N, 16.67%).

1-methyl-2-nitro-3-(pent-4-enyl)pyrrole (5 ad'): ^{1}H-NMR ($CDCl_3$) δ 2.00-2.30 (m, 4H, CH_2CH_2); 2.82 (t, 2H, CH_2, J=7.50 Hz); 3.95 (s, 3H, NMe); 5.00-5.20 (m, 2H, =CH_2); 5.66-5.89 (m, 1H, CH=); 6.00 (d, 1H, H-4, $J_{4,5}$ = 3.60 Hz); 6.61 (d, 1H, H-5); ν 1545 and 1350 (NO_2), 1140 (C=C) cm^{-1}.

1-methyl-2-nitro-5-(pent-4-enyl)pyrrole (6 ad'): ^{1}H-NMR ($CDCl_3$) δ 2.00-2.30 (m, 4H, CH_2CH_2); 2.59 (t, 2H, CH_2, J=7.50 Hz); 3.86 (s, 3H, NMe); 5.00-5.20 (m, 2H, =CH_2); 5.59-5.86 (m, 1H, CH=); 5.90 (d, 1H, H-4, $J_{4,3}$ = 4.45 Hz); 7.03 (d, 1H, H-3); ν 1545 and 1350 (NO_2), 1440 (C=C) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 61.90; H, 7.20; N, 14.40% ($C_{10}H_{14}N_2O_2$ requires C, 61.86; H, 7.22; N, 14.43%).

1-benzyl-3-methyl-2-nitropyrrole (5 ba'): ^{1}H-NMR ($CDCl_3$) δ 2.45 (s,3H, Me); 5.57 (s, 2H, CH_2); 6.24 (d, 1H, H-4, $J_{4,5}$ = 2.85 Hz); 6.80 (d, 1H, H-5); 7.25-7.38 (m, 5H, Ph); ν 1545 and 1345 (NO_2) cm^{-1}.

1-benzyl-5-methyl-2-nitropyrrole (6 ba'): ^{1}H-NMR ($CDCl_3$) δ 2.45 (s,3H, Me); 5.52 (s, 2H, CH_2); 6.10 (d, 1H, H-4, $J_{4,3}$ = 4.30 Hz); 6.88 (d, 1H, H-3); 7.25-7.38 (m, 5H, Ph); ν 1545 and 1345 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 66.70; H, 5.60; N, 12.90% ($C_{12}H_{12}N_2O_2$ requires C, 66.67; H, 5.56; N, 12.96%).

1-benzyl-2-nitro-3-isopropylpyrrole (5 bc'): ^{1}H-NMR ($CDCl_3$) δ 1.25 (d, 6H, CH_3, J=6.84 Hz); 2.90 (m, 1H, CH); 5.68 (s, 2H, CH_2); 6.17 (d, 1H, H-4, $J_{4,5}$ = 2.70 Hz); 6.82 (d, 1H, H-5); 7.25-7.38 (m, 5H, Ph); ν 1540 and 1335 (NO_2) cm^{-1}.

1-benzyl-2-nitro-5-isopropylpyrrole (6 bc'): ^{1}H-NMR ($CDCl_3$) δ 1.25 (d, 6H, CH_3, J=6.85 Hz); 3.60 (m, 1H, CH); 5.52 (s, 2H, CH_2); 6.20 (d, 1H, H-4, $J_{4,3}$ = 4.20 Hz); 6.91 (d, 1H, H-3); 7.25-7.38 (m, 5H, Ph); ν 1540 and 1335 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 68.80; H, 6.60; N, 11.50% ($C_{14}H_{16}N_2O_2$ requires C, 68.85; H, 6.56; N, 11.47%).

3-methyl-2-nitrothiophene (5 ca'): ^{1}H-NMR ($CDCl_3$) δ 2.62 (s, 3H, Me); 6.94 (d, 1H, H-4, $J_{4,5}$ = 5.00 Hz); 7.43 (d, 1H, H-5); ν 1550 and 1340 (NO_2) cm^{-1}.

5-methyl-2-nitrothiophene (6 ca'): ^{1}H-NMR ($CDCl_3$) δ 2.53 (s, 3H, Me); 6.78 (d, 1H, H-4, $J_{4,5}$ = 3.60 Hz); 7.78 (d, 1H, H-5); ν 1550 and 1340 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 42.00; H, 3.50; N, 9.80; S, 22.30% ($C_5H_5NO_2S$ requires C, 41.96; H, 3.50; N, 9.79, S, 22.38%).

3-butyl-2-nitrothiophene (5 cb'): ^{1}H-NMR ($CDCl_3$) δ 0.92 (t, 3H, CH_3, J=6.80 Hz); 1.57-1.72 (m, 4H, CH_2CH_2); 3.03 (t, 2H, CH_2, J=9.00 Hz); 6.93 (d, 1H, H-4, $J_{4,5}$ = 5.60 Hz); 7.39 (d, 1H, H-5); ν 1540 and 1335 (NO_2) cm^{-1}.

5-butyl-2-nitrothiophene (6 cb'): ^{1}H-NMR ($CDCl_3$) δ 0.95 (t, 3H, CH_3, J=6.80 Hz); 1.39 (dt, 4H, CH_2CH_2); 2.82 (t, 2H, CH_2, J=9.00 Hz); 6.75 (d, 1H, H-4, $J_{4,3}$ = 3.70 Hz); 7.76 (d, 1H, H-3); ν 1540 and 1335 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 51.90; H, 5.95; N, 7.55, S, 17.20% ($C_8H_{11}NO_2S$ requires C, 51.89; H, 5.95; N, 7.57; S, 17.30%).

2-nitro-3-isopropylthiophene (5 cc'): ^{1}H-NMR ($CDCl_3$) δ 1.33 (d, 6H, CH_3, J=6.81 Hz); 3.96 (m, 1H, CH); 7.10 (d, 1H, H-4, $J_{4,5}$ = 6.00 Hz); 7.45 (d, 1H, H-5); ν 1540 and 1335 (NO_2) cm^{-1}.

2-nitro-5-isopropylthiophene (**6 ce'**): ^{1}H-NMR ($CDCl_3$) δ 1.29 (d, 6H, CH_3, J=6.85 Hz); 3.20 (m, 1H, CH); 6.84 (d, 1H, H-4, $J_{4,3}$ = 3.60 Hz); 7.78 (d, 1H, H-3); ν 1540 and 1335 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 49.10; H, 5.25; N, 8.20; S, 18.75% ($C_7H_9NO_2S$ requires C, 49.12; H, 5.26; N, 8.19; S, 18.71%).

3-cyclohexyl-2-nitro-thiophene (**5 ce'**): ^{1}H-NMR ($CDCl_3$) δ 1.63-2.10 (m, 11H); 7.06 (d, 1H, H-4, $J_{4,5}$ = 5.30 Hz); 7.41 (d, 1H, H-5); ν 1550 and 1345 (NO_2) cm^{-1}.

3-cyclohexyl-2-nitro-thiophene (**6 ce'**): ^{1}H-NMR ($CDCl_3$) δ 1.00-1.63 (m, 11H); 6.78 (d, 1H, H-4, $J_{4,3}$ = 3.60 Hz); 7.76 (d, 1H, H-3); ν 1550 and 1345 (NO_2) cm^{-1}.

Elemental analysis of the mixture of the two isomers: Found C, 56.90; H, 6.15; N, 6.60; S, 15.20% ($C_{10}H_{13}NO_2S$ requires C, 56.87; H,6.16; N, 6.63, S, 15.17%).

2-methyl-3-nitro-1-(tri-isopropylsilyl)pyrrole (**9 aa'**): oil; ^{1}H-NMR ($CDCl_3$) δ 1.14 (d, 18H, Me, J=8.60 Hz); 1.52 (m, 3H, CH); 2.68 (s, 3H, Me); 6.58 (d, 1H, H-4, $J_{4,5}$=2.50 Hz); 6.81 (d, 1H, H-5); IR (film) ν 1550 and 1335 (NO_2); 1245 (CSi) cm^{-1}; found C, 59.60; H, 9.30; N, 9.90% ($C_{14}H_{26}N_2O_2Si$ requires C, 59.57;H, 9.22; N, 9.93%).

2-butyl-3-nitro-1-(tri-isopropylsilyl)pyrrole (**9 ab'**): oil; ^{1}H-NMR ($CDCl_3$) δ 0.96 (t, 3H, Me, J=6.80 Hz); 1.07 (d, 18H, Me, J=9.00 Hz); 1.28 (m, 3H, CH); 1.65-1.40 (m, 4H, CH_2CH_2); 2.95 (t, 2H, CH_2, J=7.50 Hz); 6.54 (d, 1H, H-4, $J_{4,5}$=2.60 Hz); 6.82 (d, 1H, H-5); IR (film) ν 1545 and 1330 (NO_2); 1240 (CSi) cm^{-1}; found C, 63.00; H, 9.90; N, 8.70% ($C_{17}H_{32}N_2O_2Si$ requires C, 62.96;H, 9.88; N, 8.64%).

3-nitro-2-isopropyl-1-(tri-isopropylsilyl)pyrrole (**9 ac'**): oil; ^{1}H-NMR ($CDCl_3$) δ 1.09 (d, 6H, Me, J=6.80 Hz); 1.18 (d, 18H, Me, J=9.00 Hz); 1.50 (m, 3H, CH); 3.10 (m, 1H, CH); 6.52 (d, 1H, H-4, $J_{4,5}$=2.80 Hz); 6.84 (d, 1H, H-5); IR (film) ν 1540 and 1335 (NO_2); 1240 (CSi) cm^{-1}; found C, 62.00; H, 9.70; N, 9.00% ($C_{16}H_{30}N_2O_2Si$ requires C, 61.94;H, 9.68; N, 9.03%).

2-methyl-3-nitrothiophene (**9 ba'**): mp 61-63 °C (lit. 62-63 °C)[13]; ^{1}H-NMR ($CDCl_3$) δ 2.80 (s, 3H, Me); 7.03 (d, 1H, H-4, $J_{4,5}$=1.70 Hz); 7.58 (d, 1H, H-5); IR (film) ν 1550 and 1330 (NO_2) cm^{-1}; found C, 41.90; H, 3.45; N, 9.75; S, 22.40% ($C_5H_5NO_2S$ requires C, 41.96; H, 3.50; N, 9.79, S, 22.38%).

3-nitro-2-isopropylthiophene (**9 bc'**): oil; ^{1}H-NMR ($CDCl_3$) δ 1.37 (d, 6H, Me, J=6.30 Hz); 4.10 (m, 1H, CH); 7.08 (d, 1H, H-4, $J_{4,5}$=1.70 Hz); 7.58 (d, 1H, H-5); IR (film) ν 1550 and 1330 (NO_2) cm^{-1} found C, 49.15; H, 5.30; N, 8.15; S, 18.70% ($C_7H_9NO_2S$ requires C, 49.12; H, 5.26; N, 8.19; S, 18.71%).

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