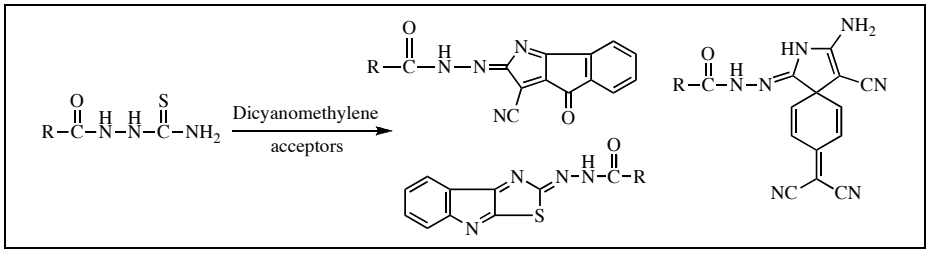
Dicyanomethylene Compounds and Heterocyclization of Acylthiosemicarbazides

Alaa A. Hassan*, Aboul-Fetouh E. Mourad and Ashraf H. Abou-Zeid

Chemistry Department, Faculty of Science, Minia University, El-Minia, A. R. Egypt.
E-Mail: alaahassan2001@yahoo.com

Received January 26, 2007



(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**1**, in ethyl acetate solution), 3-(dicyanomethylene)-2-indolone (**2**, in ethanol/piperidine solution) and 7,7',8,8'-tetracyanoquinodimethane (**3**, in pyridine solution) act on substituted acylthiosemicarbazides **4a-d**, forming the derivatives of oxoindenopyrrolylidenehydrazide (**5a-d** and **7a-d**), thiazoloindolylidenehydrazide (**12a-d**), pyrroloindolylidenehydrazide (**13a-d**) and spiro[pyrrolylidene-4,1'(cyclohexa-2',5'-dienylidene)]propanedinitrile (**18a-d**). Rationales for these conversiones involving the nucleophilic addition on dicyanomethylene carbon atom are presented.

J. Heterocyclic Chem., **45**, 323 (2008).

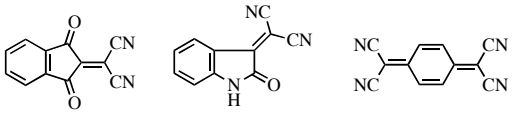
INTRODUCTION

Selective combination of two or more different electron accepting functional groups into one molecule leads to a series of new electron acceptors with unique properties. Such a composite acceptor is (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**1**), also referred to as 2-(dicyanomethylene)-1,3-indanedione [1], may be considered as a strong organic π-acid [2]. It readily adds nuclephiles such as aromatic and aliphatic amines at the dicyanomethylene carbon atom with release of hydrogen cyanide [3-7]. Acceptor (**1**) is also able to generate iminum ions from the tertiary cyclic amines and formation the α-cyanated amines [8]. Additionally, the reaction of **1** with arylazoaminopyrazoles [9,10], 2-mercaptobenzazoles [11], thiocarbohydrazide and thiocarbazones [12] as well as *N*-arylisoindolines [13] have been reported.

Closely analogous 3-(dicyanomethylene)-2-indolone (**2**) [14] which is a ylidenemalononitrile like **1** reacted with ketene *S*,*S*- and *N*,*S*-acetals [15], active methylene compounds [16-20] and cyclohexanedione [21] to give spiro heterocyclic compounds. The reaction of *N*,*N*'-diarylacetamidines with **1** afforded indenoazepine-6-ones [22]. In contrast, spiro[2,3-dihydroindol-3,4'-pyridino]-5'-carbonitriles were obtained from the reaction of *N*,*N*'-diarylacetamidines with **2** [22].

Encouraged by these results, in the present work we describe the chemical behaviour of acylthiosemicarbazides **4a-d** towards acceptor systems **1-3**.

Chart 1



1 **2** (TCNQ, **3**)

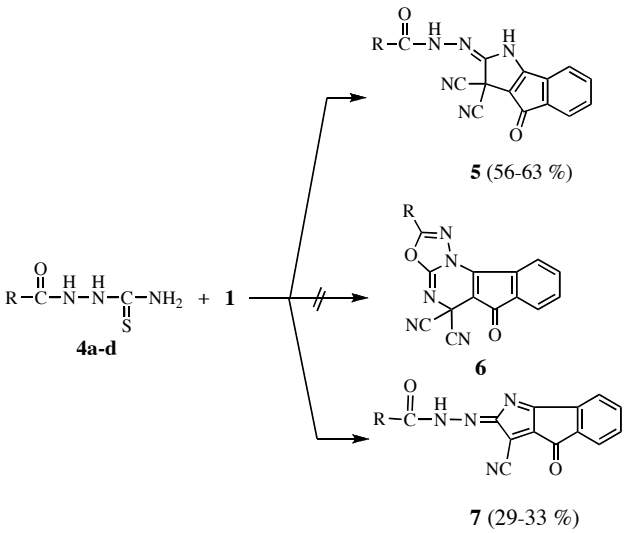
RESULTS AND DISCUSSION

Treatment of **4a-d** with two molar equivalents of (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**1**) in ethyl acetate as solvent at room temperature resulted in a yellow colouration of the solution which later became brown. Concentration of the reaction mixture yielded a brown precipitate **5** (56-63 %). The remaining soluble materials were subjected to preparative layer chromatography. From the one significant yellow zone and by crystallization, the *N*'-(3-cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene) substituted hydrazides **7** were obtained in 29-33 % yield.

The IR spectrum of **5b** shows absorption bands characteristic of NH groups at 3395, 3210, strong cyano groups at 2210, two carbonyl absorption at 1735 and 1675 cm^{-1}. ^{1}H-NMR spectrum of **5b** clearly supports the presence of two different broad signals centered at δ 11.12 and 11.28 ppm due to the amide-NH and pyrrole-NH, respectively. In the ^{13}C-NMR spectrum the carbonyl groups of benzohydrazide and oxoindeno C-4 resonate at δ = 174.12 and 182.12 ppm, respectively. Further peaks at 116.11 ppm (CN), at 155.63 (pyrrole-C2) and 60.12 ppm (pyrrole-C3), besides the aromatic carbons support the

assigned structure. Elemental analysis of **5b** suggested a gross formula $C_{20}H_{11}N_5O_2$. This was also confirmed by the mass spectrum which exhibited the molecular ion at m/z 353 (12 %). It is worthy to note that the mass spectra of compounds **5a-d** show the loss of $C(CN)_2$ as well as the acyl group from the molecular ions. The alternative structure **6** could be ruled out on the basis of IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Scheme 1

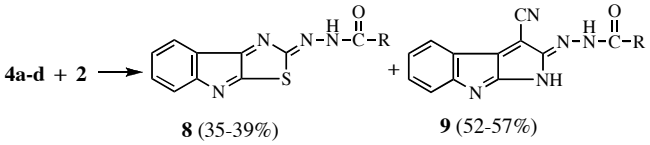


4,5,7: a, R = CH_3-; **b**, R = C_6H_5-; **c**, R = 4-HO-C_6H_4-; **d**, R = 4-Br-C_6H_4-CH_2-

For the formation of oxoindenopyrrolylidene derivatives **7a-d**, the mass spectrum as well as elemental analysis of **7b** established the molecular formula $C_{19}H_{10}N_4O_2$. The IR spectrum showed the carbonyl groups at 1735 and 1670 cm^{-1}. These carbonyl groups appeared at δ = 172.63 for the amide carbonyl group and δ = 183.12 for oxoindeno-C4, in the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum of **7b** showed one broad signal at δ = 11.10 ppm (NH) in addition to the aromatic protons. In the ^{13}C-NMR spectrum the pyrrole-C-2, C-3, C-4 and C-8b absorb at δ = 156.12, 124.17, 183.12 and 164.35, respectively. Also, the ^{13}C-NMR of **7b** clearly indicates the presence of one cyano group at 118.47 ppm beside the aromatic carbons.

The weaker acceptor **2**, being easily accessible from isatine [14], was expected to react similarly to **1** with the acylthiosemicarbazides **4a-d**. Reflux of one mole of **4a-d** with two equivalents of **2** in ethanol/piperidene resulted in pink colouration of the solution, which later became pale brown. The residue remaining after concentration was subjected to preparative layer chromatography to give substituted thiazoloindolylidene **8a-d** (35-39 %) and substituted pyrroloindolylidene **9a-d** (52-57 %) (Scheme 2).

Scheme 2



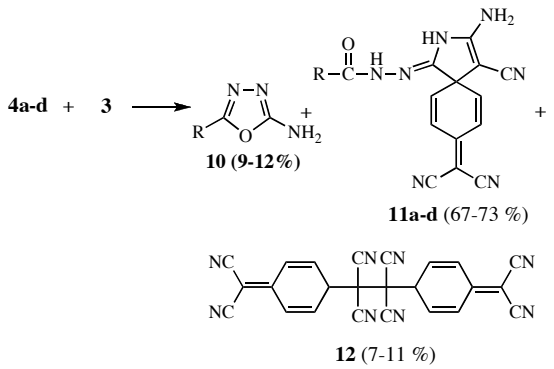
4,8,9: a, R = CH_3-; **b**, R = C_6H_5-; **c**, R = 4-HO-C_6H_4-; **d**, R = 4-Br-C_6H_4-CH_2-

The IR spectra of **8a-d** in KBr disc shows absorption characteristic of NH groups at 3350-3375, and carbonyl group at 1690-1700 cm^{-1}. The ^{1}H-NMR spectrum of **8a** clearly shows the presence of aryl protons and amide-NH. The ^{13}C-NMR of **8a** shows signals at 154.92, 164.22 and 163.28 due to thiazole-C-2, C-8a and C-3a, respectively and at 173.44 for (CO) in addition to the aryl carbons. The molecular formulae of compounds **8a-d** are supported by elemental analysis and mass spectra which gave the expected molecular ion peaks.

Compounds **9a-d** show a characteristic yellow colour. The gross formula of **9b** was confirmed by the mass spectrum, which exhibited the molecular ion at m/z 313 (26 %). The IR spectrum showed absorption at 3395 and 3210 (NH), 2215 (CN), and 1695 cm^{-1} (CO). The ^{1}H-NMR spectrum of **9b** displayed two broad signals at 11.12 ppm for amide-NH and 11.33 ppm for pyrrole-NH in addition to the aromatic protons. In it's ^{13}C-NMR spectrum C-2, C-3, C-8a and C-3a resonate at δ = 156.73, 112.36, 164.22 and 148.69 ppm, respectively; further peaks are at δ = 173.94 (CO) and 118.14 (CN).

7,7,8,8-Tetracyanoquinodimethane (TCNQ, **3**) is very well-known electron-acceptor molecule [23], which has been successfully used for the preparation of electrically conducting salts and CT-complexes [24]. The interest of TCNQ has been focused on it's potential applications on molecular rectifiers [25], nonlinear optical materials [26], organic ferromagents [27] and organic chromophores with electron accepting properties [28]. Recently, it has been found that the addition of 1,8-diaminonaphthalene to

Scheme 3



4,10,11: a, R = CH_3-; **b**, R = C_6H_5-; **c**, R = 4-HO-C_6H_4-; **d**, R = 4-Br-C_6H_4-CH_2-

TCNQ (**3**) afforded 2-[4-(1*H*,3*H*-pyrimidin-2-ylidene)-cyclohexa-2,5-dienylidene]malononitrile [29].

Pyridine solution of TCNQ (**3**) and **4a-d** in a molar ratio of 2:1 were kept at 100 °C for 2 hours with admission of air. Chromatographic separation of the residue after concentration gave numerous coloured zones, from which products **11a-d** could be isolated. In addition, the known compounds **10a-c** [30-34], **12** [35] were found in small quantities in all cases.

Structural assignment of products **11a-d** is based on spectral data and on combustion analysis. The elemental analysis of **11b** supporting the gross formula $C_{20}H_{13}N_7O$, and the mass spectrum which gave a correct molecular ion at m/z 367 (17%). The IR spectrum of **11b** showed NH_2 and NH absorption bands at ν = 3425 and 3330-3240, cyano groups at 2215, 2220, and carbonyl group at 1690 cm^{-1}. The ^{1}H-NMR spectrum revealed three broad signals with the ratio 2:1:1 at δ = 8.16, 11.10 and 11.31 related to NH_2, amide-NH and pyrrole-NH, respectively. The ^{13}C-NMR spectrum of **11b** confirmed its ^{1}H-NMR spectral data by the appearance of signals at 48.63 (q-C-4), 64.12 (pyrrole-C-3), 74.18 (C-7'), 156.21 (C-5), 164.93 (C-2) and 174.39 (CO). The analytical data of compound **11** could also match for other isomers of products **13-15** (Figure 1).

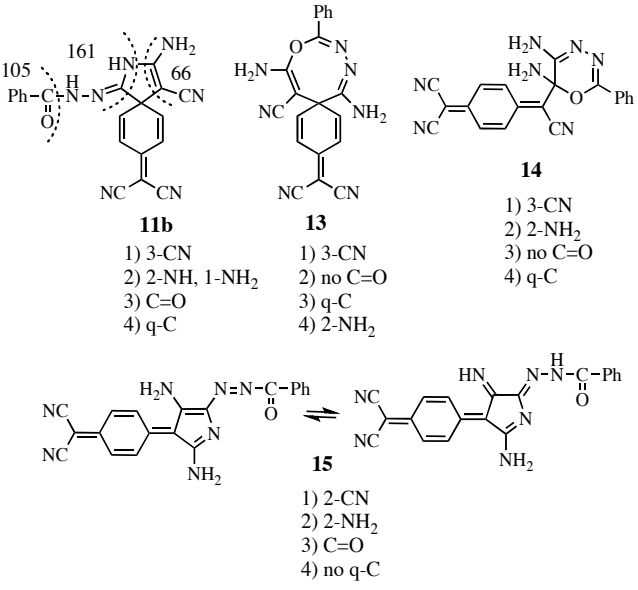
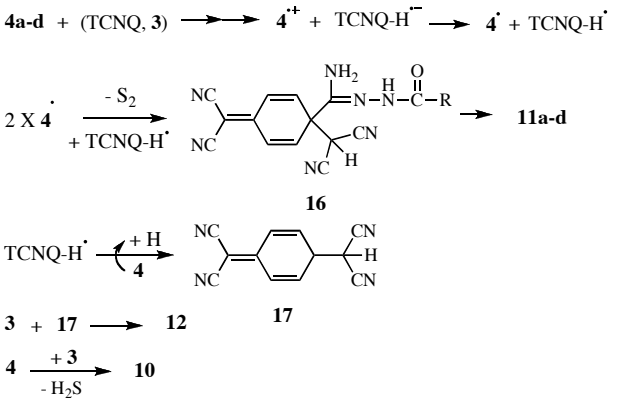


Figure 1

The alternative structures **13-15** could also be ruled out on the basis of ^{1}H-NMR, ^{13}C-NMR and the fragment ions in the mass spectrum of **11b** at m/z 303, 237, 206, 105 and 66. As shown in Figure 1, structure **11b** fits best to all the spectroscopic data (see experimental section). Formation of the spiro compounds **11a-d** derived from TCNQ may be rationalizes as out lined in Scheme 4.

Scheme 4



CONCLUSION

The reactions and products presented here provide insight into the spontaneous reactions between the electron donors 1-acylthiosemicarbazides **4a-d** and electron acceptors (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**1**), 3-(di-cyanomethylene)-2-indolone (**2**) and 7,7,8,8-tetracyanoquinodimethane (TCNQ, **3**). In a fairly complex and multistep process, fused heterocyclic and spiro[pyrrolylidene-4,1'-(cyclohexa-2',5'-dienylidene)]propanedinitrile products are formed from **4a-d** and **1**, **2** or **3**. The predominant products **5**, **7**, **8** and **9** have an intenesting fused heterocyclic systems. Further, compounds **11a-d** resemble analogues of the family of heterocyclic tetracyanoquinodimethanes [29,36,37]. The results reported here supplement the rich chemistry of 1-acylthiosemicarbazides **4a-d**.

EXPERIMENTAL

Mp's were determined with a Gallenkamp melting point apparatus and are uncorrected. The IR specra were recorded with a Shimadzue 408 or a Bruker Vector 22 FT-IR spectrometers using potassium bromide pellets. ^{1}H 300 MHz and ^{13}C NMR 75 MHz spectra were recorded on a Bruker WM 300 instrument, 500 MHz ^{1}H and 125 MHz ^{13}C NMR spectra on a Bruker DRX 500 spectrometer. Chemical shifts are expressed as δ [ppm] with reference to tetramethylsilane as an internal standard, s = singlet, d = doublet, m = multiplet. ^{13}C assignments (qC = quaternary carbon atoms) were made with the aid of DEPT 135/90 spectra for compound **5a,d**, **7a,d**, **8a,d**, **9a,d** and **11a,d**. The mass spectra (70 eV, electron impact mode) were recorded on an AMD 604 instrument. Elemental analyses were carried out at the microanalytical center, Cairo University, Egypt. For preparative layer chromatography (plc) 1.0 mm thick air-dried layers of slurry applied silica gel Merck Pf_{254} on 48 cm wide and 20 cm high glass plates were used, zones were detected by their colour and indicator fluorescence quenching upon exposure to 254 nm light and extracted with acetone.

Starting Materials. 1-Acylthiosemicarbazides **4a-c** were prepared according to the procedures published in literature. The ^{1}H-NMR spectral data of **4a-c** were in full accord with the published data.

1-Acetylthiosemicarbazide **(4a)**; m.p = 165-167 °C (lit. [38] 166 °C). **1-**Benzoylthiosemicarbazide **(4b)**; m.p = 195-197 °C (lit. [39] 196-199 °C. 1-(4-Hydroxyphenzoyl)thiosemicarbazide **(4c)**; m.p = 212-214 °C (lit. [40] 214-216 °C).

1-(4-Bromo-phenylacetyl)thiosemicarbazide (4d). To a srirred solution of thiosemicarbazide (0.91 g, 10 mmol) in 50 ml dry acetone, *p*-bromophenylacetic acid (2.15 g, 10 mmol) was added and the mixture was refluxed for 3 hours. A white precipitate was formed, recrystallized from ethanol to give colourless crystals (2.84 g, 85 %), m.p = 93-95 °C.

2-(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile(dicyanomethyleneindane-1,3-diane (1) was prepared according to Chatterjee [1]. 3-(Dicyanomethylene)-2-indolone (**2**) was prepared according to Fatiadi [14]. 7,7,8,8-Tetracyanoquinodimethane (TCNQ, **3**) was bought from Merck.

Reaction of 1-acylthiosemicarbazides 4a-d with (1). To a solution of 1.0 mmol of **4a-d** in 20 ml ethyl acetate 416 mg (2.0 mmol) of (**1**) were added within two minutes, the initially yellow solution first turned red and then brown and was stirred for 3 h at 20 °C. The mixture was left standing for 48 h at room temperature, after which time a brown precipitate of **5a-d** was collected and crystallized. The mother liquor was separated by plc using cyclohexane/ethyl acetate (1:1) to give a reddish orange colour zone contaning compounds **7a-d**.

***N*'-(3,3-Dicyano-4-oxoindeno[1,2-*b*]pyrrol-2(1*H*,3*H*,4*H*)-ylidene)acetohydrazide (5a).** This compound was obtained as brown crystals (acetonitrile), mp 215-217°; ir: NH 3385, 3200, CN 2215, CO 1730, 1670, aryl 1590 cm^{-1}; ^1H nmr: δ 2.36 (s, 3H, CH_3), 7.53-8.10 (m, 4H, aryl H), 11.08 (br, 1H, amide-NH); 11.25 (br, 1H, pyrrole-NH); ^{13}C nmr: δ 20.79 (CH_3), 59.78 (C-3), 116.14 (CN), 124.81 (C-3a), 127.81, 128.44, 132.24, 132.71 (aryl-CH), 134.75, 137.33 (aryl-C), 156.18 (C-8b), 155.76 (C-2), 170.38 (amide-CO), 181.89 (C-4); ms: *m/z* 291 (M^+, 16), 227 (31), 199 (18), 178 (22), 135 (36), 105 (61), 43 (100), 15 (97). *Anal.* Calcd. for $C_{15}H_9N_5O_2$: C, 61.85; H, 3.11; N, 24.04. Found: C, 62.03; H, 2.96; N, 24.19.

***N*'-(3,3-Dicyano-4-oxoindeno[1,2-*b*]pyrrol-2(1*H*,3*H*,4*H*)-ylidene)benzohydrazide (5b).** This compound was obtained as brown crystals (acetonitrile), mp 263-265°; ir: NH 3395, 3210, CN 2210, CO 1735, 1675, aryl 1600 cm^{-1}; ^1H nmr: δ 7.11-8.18 (all m, 9H, aryl H), 11.12 (br, 1H, amide-NH); 11.28 (br, 1H, pyrrole-NH); ^{13}C nmr: δ 60.12 (C-3), 116.11 (CN), 124.48 (C-3a), 127.51, 127.83, 128.46, 128.90, 132.22, 132.62 (aryl-CH), 134.28, 134.79, 137.39 (aryl-C), 156.28 (C-8b), 155.63 (C-2), 174.12 (amide-CO), 182.12 (C-4); ms: m/z 353 (M^+, 12), 289 (33), 261 (18), 156 (44), 105 (100), 77 (67), 65 (53). *Anal.* Calcd. for $C_{20}H_{11}N_5O_2$: C, 67.99; H, 3.14; N, 19.82. Found: C, 67.81; H, 3.26; N, 20.03.

***N*'-(3,3-Dicyano-4-oxoindeno[1,2-*b*]pyrrol-2(1*H*,3*H*,4*H*)-ylidene)-4-hydroxybenzohydrazide (5c).** This compound was obtained as red crystals (acetonitrile), mp 275-277°; ir: OH, NH 3460-3220, CN 2220, CO 1730, 1675, aryl 1610 cm^{-1}; ^1H nmr: δ 6.98-8.11 (all m, 8H, aryl H), 9.12 (br, 1H, OH), 11.08 (br, 1H, amide-NH); 11.27 (pyrrole-NH); ^{13}C nmr: δ 59.12 (C-3), 116.22 (CN), 124.66 (C-3a), 126.11, 126.33, 127.55, 128.46, 132.18, 132.44 (aryl-CH), 134.33, 134.72, 157.62 (aryl-C), 156.83 (C-8b), 155.43 (C-2), 173.58 (amide-CO), 181.89 (C-4); ms: m/z 369 (M^+, 21), 352 (18), 305 (26), 277 (11), 172 (22), 121 (100), 105 (86), 93 (76), 77 (56). *Anal.* Calcd. for $C_{20}H_{11}N_5O_3$: C, 65.04; H, 3.00; N, 18.96. Found: C, 64.64; H, 2.88; N, 19.18.

2-(4-Bromophenyl)-*N*'-(3,3-dicyano-4-oxoindeno-[1,2-*b*]-pyrrol-2(1*H*,3*H*,4*H*)-ylidene)acetohydrazide (5d). This compound was obtained as brown crystals (acetonitrile), mp 185-187°; ir: NH 3390, 3220, CN 2220, CO 1730, 1670, aryl 1610 cm^{-1}; ^1H nmr: δ 4.31 (s, 2H, CH_2), 6.95-8.10 (m, 8H, aryl H), 11.06 (br, 1H, amide-NH); 11.26 (br, 1H, pyrrole-NH); ^{13}C nmr: δ 52.76 (CH_2), 116.71 (CN), 124.95 (C-3a), 126.92, 126.91, 127.44, 128.28, 132.11, 132.34 (aryl-CH), 132.18, 134.19, 135.16 (aryl-C), 155.64 (C-2), 156.67 (C-8b), 174.12 (amide-CO), 182.13 (C-4); ms: m/z 447/445 (M^+, 21), 365 (76), 260 (28), 198 (43), 105 (61), 90 (100), 77 (74), 65 (44). *Anal.* Calcd. for $C_{21}H_{12}BrN_5O_2$: C, 56.52; H, 2.70; Br, 17.91; N, 15.69. Found: C, 56.71; H, 2.57; Br, 18.11; N, 15.53.

***N*'-(3-Cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)-acetohydrazide (7a).** This compound was obtained as brown crystals (ethanol), mp 196-198°; ir: NH 3360, CN 2220, CO 1730, 1660, C=N 1610, aryl 1585 cm^{-1}; ^1H nmr: δ 2.38 (s, 3H, CH_3), 7.61-7.82 (m, 4H, aryl-H), 11.05 (br, 1H, amide-NH) ; ^{13}C nmr: δ 20.67 (CH_3), 118.12 (CN), 124.13 (C-3), 129.76, 130.24, 131.62, 132.42 (aryl-CH), 134.79, 139.32 (aryl-C), 149.75 (C-3a), 155.78 (C-2), 164.16 (C-8b), 173.88 (amide-CO), 182.72 (C-4); ms: m/z 264 (M^+, 23), 221 (32), 195 (24), 167 (12), 139 (22), 105 (73), 43 (100). *Anal.* Calcd. for $C_{14}H_8N_4O_2$: C, 63.64; H, 3.05; N, 21.20. Found: C, 63.48; H, 2.87; N, 21.39.

***N*'-(3-Cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)benzohydrazide (7b).** This compound was obtained as yellow crystals (acetonitrile), mp 240-242°; ir: NH 3385, CN 2220, CO 1735, 1670, C=N 1620, aryl 1600 cm^{-1}; ^1H nmr: δ 7.24-7.88 (m, 4H, aryl-H), 11.10 (br, 1H, amide-NH); ^{13}C nmr: δ 118.47 (CN), 124.17 (C-3), 128.56, 129.96, 130.12, 130.74, 131.66, 132.24, 132.46 (aryl-CH), 134.76, 134.93, 139.68 (aryl-C), 149.66 (C-3a), 156.12 (C-2), 164.35 (C-8b), 172.63 (amide-CO), 183.12 (C-4); ms: m/z 326 (M^+, 19), 300 (16), 272 (21), 244 (8), 221 (26), 105 (100), 77 (63), 65 (54). *Anal.* Calcd. for $C_{19}H_{10}N_4O_2$: C, 69.93; H, 3.09; N, 17.17. Found: C, 70.12; H, 2.86; N, 16.95.

***N*'-(3-Cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)4-hydroxybenzohydrazide (7c).** This compound was obtained as brown crystals (methanol), mp 265-267°; ir: OH, NH 3430-3370, CN 2215, CO 1735, 1660, C=N 1620, aryl 1595 cm^{-1}; ^1H nmr: δ 6.96-7.82 (m, 8H, aryl-H), 9.36 (br, 1H, OH), 11.10 (br, 1H, amide-NH); ^{13}C nmr: δ 118.22 (CN), 124.12 (C-3), 126.18, 127.93, 128.96, 129.76, 130.26, 131.66, 132.48 (aryl-CH), 134.78, 139.96, 139.94, 161.94 (aryl-C), 149.70 (C-3a), 156.12 (C-2), 156.12 (C-2), 164.63 (C-8b); ms: m/z 342 (M^+, 22), 316 (14), 288 (7), 221 (19), 121 (100), 105 (79), 92 (83), 77 (62), 65 (46). *Anal.* Calcd. for $C_{19}H_{10}N_4O_3$: C, 66.67; H, 2.94; N, 16.36. Found: C, 66.49; H, 3.06; N, 16.53.

2-(4-Bromophenyl)-*N*'-(3-cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)benzohydrazide (7d). This compound was obtained as red crystals (methanol), mp 160-162°; ir: NH 3375, CN 2210, CO 1730, 1660, C=N 1615, aryl 1585 cm^{-1}; ^1H nmr: δ 4.28 (s, 2H, CH_2), 6.94-7.86 (m, 8H, aryl-H), 11.05 (br, 1H, amide-NH) ; ^{13}C nmr: δ 52.46 (CH_2), 117.93 (CN), 123.86 (C-3), 126.10, 127.66, 129.92, 130.28, 131.67, 132.12, 132.64 (aryl-CH), 134.76, 137.92, 139.84 (aryl-C), 149.56 (C-3a), 155.88 (C-2), 164.69 (C-8b), 174.44 (amide-CO), 183.12 (C-4); ms: m/z 420/ 418 (M^+, 34), 392 (12), 364 (9), 284 (24), 233 (21), 198 (73), 105 (100), 91 (81), 77 (63), 65 (54). *Anal.* Calcd. for $C_{20}H_{11}BrN_4O_2$: C, 57.30; H, 2.64; Br, 19.06; N, 13.36. Found: C, 57.18; H, 2.76; Br, 18.82, N, 13.54.

Reaction of acylthiosemicarbazides 4a-d with 2. 1-Acyl-thiosemicarbazides **4a-d** (1 mmol) were dissolved in 20 ml absolute ethanol with two drops of piperidine and added to the indolone **2** (2 mmol) in 25 ml ethanol, the mixture was heated

under reflux for 15 h, cooled to room temperature, concentrated and subjected to plc using cyclohexane/ethyl acetate (1:1) to give numerous coloured zones, the two intense of which were removed and extracted. The fastest migrating one contained the thiazoloindolylidenehydrazide derivatives **8a-d**. The slowest migrating zone (which is always characterized by yellow colour) contained pyrroloindolylidene hydrazide derivatives **9a-d**. Extraction of the zones with acetone and crystallized.

***N*'-(2*H*-Thiazolo[5,4-*b*]indol-2-ylidene]acetohydrazide (8a).** This compound was obtained as brown crystals (acetonitrile), mp 214-216°; ir: NH 3360, CO 1690, C=N 1620, aryl 1580 cm^{-1}; ^1H nmr: δ 2.36 (s, 2H, CH_3), 7.37-7.68 (m, 4H, aryl-H), 11.08 (br, 1H, amide-NH); ^{13}C nmr: δ 21.31 (CH_3), 127.93, 128.14, 129.22, 130.51 (aryl-CH), 134.77, 149.56 (aryl-C), 154.92 (C-2), 163.28 (C-8b), 164.22 (C-3a), 173.44 (amide-CO); ms: m/z 244 (M^+, 26), 201 (22), 109 (53), 91 (38), 77 (54), 43 (100), 28 (29). *Anal*. Calcd. for $C_{11}H_8N_4O_5$: C, 54.09; H, 3.30; N, 22.94; S, 13.13. Found: C, 53.89; H, 3.49; N, 23.17; S, 13.32.

***N*'-(2*H*-Thiazolo[5,4-*b*]indol-2-ylidene]benzohydrazide (8b).** This compound was obtained as brown crystals (methanol), mp 233-235°; ir: NH 3375, CO 1695, C=N 1610, aryl 1600 cm^{-1}; ^1H nmr: δ 7.24-7.72 (m, 9H, aryl-H), 11.10 (br, 1H, amide-NH); ^{13}C nmr: δ 127.66, 127.93, 129.13, 130.63, 132.12 (aryl-CH), 134.54, 134.61, 149.76 (aryl-C), 155.13 (C-2), 163.76 (C-8b), 164.62 (C-3a), 172.14 (amide-CO); ms: m/z 306 (M^+, 16), 278 (9), 171 (24), 135 (53), 105 (100), 77 (67), 65 (48). *Anal*. Calcd. for $C_{16}H_{10}N_4O_5$: C, 62.73; H, 3.29; N, 18.29; S, 10.47. Found: C, 62.51; H, 3.16; N, 18.11; S, 10.66.

4-Hydroxy-*N*'-(2*H*-thiazolo[5,4-*b*]indol-2-ylidene]benzohydrazide (8c). This compound was obtained as brown crystals (acetonitrile), mp 274-276°; ir: OH, NH 3420-3350, C=O 1700, C=N 1625, aryl 1600 cm^{-1}; ^1H nmr: δ 6.92-7.78 (aryl-H), 9.23 (br, 1H, OH), 11.05 (br, 1H, amide-NH), ^{13}C nmr: δ 126.22, 127.46, 128.93, 130.54, 130.96, 131.14 (aryl-CH), 134.61, 149.58, 161.92 (aryl-C), 155.13 (C-2), 163.26 (C-8a), 164.53 (C-3a), 173.12 (amide-CO); ms: m/z 322 (M^+, 16), 305 (5), 294 (16), 201 (34), 135 (26), 121 (73), 93 (100), 77 (71), 65 (62). *Anal*. Calcd. for $C_{16}H_{10}N_4O_2S$: C, 59.62; H, 3.13; N, 17.38; S, 9.95. Found: C, 59.46; H, 2.98; N, 17.56; S, 10.14.

2-(4-Bromophenyl-*N*'-(2*H*)-thiazolo[5,4-*b*]indol-2-ylidene]-acetohydrazide (8d). This compound was obtained as brown crystals (ethanol), mp 181-183°; ir: NH 3355, C=O 1690, C=N 1620, aryl 1590 cm^{-1}; ^1H nmr: δ 4.28 (s, 2H, CH_2), 6.91-7.77 (m, 8H, aryl), 11.05 (br, 1H, amide-NH); ms: m/z 400/ 398 (M^+, 22), 318 (19), 198 (42), 135 (24), 118 (37), 91 (74), 77 (100), 65 (52). *Anal*. Calcd. for $C_{17}H_{11}BrN_4OS$: C, 51.14; H, 2.78; Br, 20.01; N, 14.03; S, 8.03. Found: C, 51.31; H, 2.91; Br, 19.86; N, 13.84; S, 8.21.

***N*'-(3-Cyanopyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)acetohydrazide (9a).** This compound was obtained as yellow crystals (ethanol), mp 186-188°; ir: NH 3380, 3190, CN 2220, C=O 1685, C=N 1620, aryl 1600 cm^{-1}; ^1H nmr: δ 2.40 (s, 3H, CH_3), 7.42-7.81 (m, 4H, aryl-H), 11.08 (br, 1H, amide-NH), 11.31 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 21.76 (CH_3), 112.62 (C-3), 117.32 (CN), 127.92, 128.22, 129.36 (aryl-CH), 132.12, 146.76 (aryl-C), 148.56 (C-3a), 156.24 (C-2), 164.18 (C-8a), 173.71 (CO); ms: m/z 251 (M^+, 31), 225 (13), 148 (27), 103 (41), 43 (100), 28 (53). *Anal*. Calcd. for $C_{13}H_9N_5O$: C, 62.15; H, 3.61; N, 27.87. Found: C, 62.37; H, 3.42; N, 28.11.

***N*'-(3-Cyanopyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)benzohydrazide (9b).** This compound was obtained as yellow crystals (acetonitrile), mp 204-206°C; ir: NH 3395, 3210, CN 2215, C=O 1695, C=N 1620, aryl 1595 cm^{-1}; ^1H nmr: δ 7.12-7.94 (m, 9H, aryl-H), 11.12 (br, 1H, amide-NH), 11.33 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 118.14 (CN), 112.36 (C-3), 127.35, 127.76, 127.83, 128.94, 129.36, 130.24 (aryl-CH), 132.36, 146.76 (aryl-C), 148.69 (C-3a), 156.73 (C-2), 164.22 (C-8a), 173.94 (CO); ms: m/z 313 (M^+, 26), 287 (14), 259 (6), 208 (26), 105 (100), 103 (87), 91 (81), 77 (63), 65 (41). *Anal*. Calcd. for $C_{18}H_{11}N_5O$: C, 69.00; H, 3.54; N, 22.35. Found: C, 68.76; H, 3.71; N, 22.11.

***N*'-(3-Cyanopyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)-4-hydroxybenzohydrazide (9c).** This compound was obtained as yellow crystals (acetonitrile), mp 241-243°; ir: OH 3435, NH 3210, CN 2220, C=O 1690, C=N 1625, aryl 1610 cm^{-1}; ^1H nmr: δ 6.92-7.83 (m, 8H, aryl-H), 9.42 (br, 1H, OH), 11.08 (br, 1H, amide-NH), 11.32 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 111.94 (C-3), 118.14 (CN), 126.13, 127.23, 127.76, 128.94, 129.33 (aryl-CH), 132.16, 133.82, 146.76, 161.93 (aryl-C), 149.76 (C-3a), 156.22 (C-2), 164.37 (C-8a), 173.88 (CO); ms: m/z 329 (M^+, 17), 312 (7), 286 (12), 258 (14), 208 (31), 121 (92), 103 (76), 93 (100), 77 (62), 65 (49). *Anal*. Calcd. for $C_{18}H_{11}N_5O_2$: C, 65.65; H, 3.37; N, 21.27. Found: C, 65.89; H, 3.51; N, 21.02.

2-(4-Bromophenyl)-*N*'-(3-cyanopyrrolo[2,3-*b*]indol-2(1*H*)-ylidene)-4-acetohydrazide (9d). This compound was obtained as orange crystals (methanol), mp 223-225°; ir = NH 3375, 3215, CN 2220, C=O 1695, C=N 1610, aryl 1585 cm^{-1}; ^1H nmr: δ 4.22 (s, 2H, CH_2), 6.92-7.44 (m, 8H, aryl-H), 11.03 (br, 1H, amide-NH), 11.26 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 52.76 (CH_2), 111.88 (C-3), 118.26 (CN), 126.12, 127.23, 127.76, 129.36, 131.94, 132.26 (aryl-CH), 130.12, 131.14, 146.76 (aryl-C), 151.36 (C-3a), 156.18 (C-2), 164.44 (C-8a), 173.28 (CO); ms: m/z 406/404 (M^+, 21), 378 (14), 298 (11), 207 (31), 179 (42), 151 (88), 91 (100), 77 (67). *Anal*. Calcd. for $C_{19}H_{12}BrN_5O$: C, 56.19; H, 2.97; Br, 19.67; N, 17.25. Found: C, 56.38; H, 2.67; Br, 19.86; N, 17.10.

Reaction of 4a-d with (TCNQ, 3). To a solution of **3** (408 mg, 2.0 mmol) in dry pyridine (15 ml) a solution of **4a-d** (1.0 mmol) in 10 ml of pyridine was added dropwise over 5 min at room temperature. The mixture was warmed gently without increasing the temperature above 100 °C and kept at this temperature with stirring and admission of air for 3 hours. The solvent was removed and concentrated to dryness at 50 °C. The residue was taken up several times with cold ethanol (10 ml) and the slurry was concentrated again to remove any residual pyridine. The residue was dissolved in acetone and separated by preparative layer chromatography using chloroform/methanol (20:1) as eluent into numerous zones, three of which were extracted. The fastest migrating zone, which quenched all indicator fluorescence upon exposure to 254 nm uv-light contained oxadiazole derivatives (**10a-d**). The material confined to the start was re-chromatographed using chloroform/methanol (10:1) to give another two zones, the faster migrating one contained (**12**), whereas the second zone (deep blue) contained **11a-d**. Extraction of the zones with acetone gave a residue, which was rechromatographed with some eluent to enhance separation. Recrystallization from suitable solvents afforded compounds **10**, **11** and **12**.

***N*'-(2-Amino-3-cyano)spiro[pyrrol-5-ylideneacetohydrazide-4,1'-(cyclohexa-2',5'-dienylidene)]propanedinitrile (11a).** This compound was obtained as blue crystals (acetonitrile), mp 296-298°; ir: NH_2 3430, NH 3320-3250, CN 2225, 2210, CO 1695, C=N 1620, aryl 1600 cm^{-1}; ^1H nmr: δ 2.39 (s, 3H, CH_3), 6.38, 6.66 (d, d, 4H, C-1,2,4,5), 8.12 (br, 2H, NH_2), 11.06 (br, 1H, amide-NH), 11.28 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 22.11 (CH_3), 48.56 (q-C-4), 63.64 (pyrrole-C-3), 74.22 (C-7'), 117.93, 119.12 (CN),

124.34, 128.89 (quino-CH), 155.93 (C=N, C-5), 164.89 (C-2), 174.18 (CO), 177.73 (C-4'); ms: m/z 305 (M^+, 26), 262 (27), 198 (22), 163 (19), 109 (26), 66 (16), 43 (100), 28 (74). *Anal*. Calcd. for $C_{15}H_{11}N_7O$: C, 59.01; H, 3.63; N, 32.12. Found: C, 58.78; H, 3.79; N, 32.36.

***N*'-(2-Amino-3-cyano)spiro[pyrrol-5-ylidenebenzohydrazide-4,1'-(cyclohexa-2',5'-dienylidene)]propanedinitrile (11b).** This compound was obtained as deep blue crystals (acetonitrile), mp 311-313°; ir: NH_2 3425, NH 3330-3240, CN 2220, 2215, CO 1690, C=N 1620, aryl 1595 cm^{-1}; ^1H nmr: δ 6.28, 6.62 (d, d, 4H, C-1,2,4,5), 7.18-7.83 (m, 5H, aryl-H), 8.16 (br, 2H, NH_2), 11.10 (br, 1H, amide-NH), 11.31 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 48.63 (q-C-4), 64.12 (pyrrole-C-3), 74.18 (C-7'), 118.11, 119.22 (CN), 124.44, 128.18 (quino-CH), 126.61, 129.74, 132.11 (aryl-CH), 134.56 (aryl-C), 156.21 (C=N, C-5), 164.93 (C-2), 174.39 (CO), 177.61 (C-4'); ms: m/z 367 (M^+, 17), 303 (21), 237 (16), 206 (6), 105 (86), 77 (100), 66 (61). *Anal*. Calcd. for $C_{20}H_{13}N_7O$: C, 65.39; H, 3.57; N, 26.09. Found: C, 65.57; H, 3.41; N, 25.82.

4-Hydroxy-*N*'-(2-amino-3-cyano)spiro[pyrrol-5-ylidene-benzohydrazide-4,1'-(cyclohexa-2',5'-dienylidene)]propane-dinitrile (11c). This compound was obtained as deep blue crystals (methanol), mp 332-334°; ir: OH 3470, NH_2 3910, NH 3325-3260, CN 2215, 2210, CO 1695, C=N 1615, aryl 1600 cm^{-1}; ^1H nmr: δ 6.31, 6.64 (d, d, 4H, C-1,2,4,5), 6.96-7.78 (m, 4H, aryl-H), 8.16 (br, 2H, NH_2), 9.36 (br, 1H, OH), 11.08 (br, 1H, amide-NH), 11.32 (br, 1H, pyrrole-NH), ^{13}C nmr: δ 48.59 (q-C-4), 63.95 (pyrrole-C-3), 74.22 (C-7'), 117.98, 119.16 (CN), 124.16, 127.72 (quino-CH), 128.11, 129.56 (aryl-CH), 134.41, 159.21 (aryl-C), 155.96 (C=N, C-5), 165.06 (C-2), 174.31 (CO), 177.42 (C-4'); ms: m/z 383 (M^+, 14), 319 (17), 262 (24), 238 (16), 225 (9), 206 (6), 121 (82), 93 (100), 77 (76), 66 (51). *Anal*. Calcd. for $C_{20}H_{13}N_7O_2$: C, 62.66; H, 3.42; N, 25.58. Found: C, 62.89; H, 3.28; N, 25.35.

2-(4-Bromophenyl)-N'-(2-amino-3-cyano)spiro[pyrrol-5-yl-idenebenzohydrazide-4,1'-(cyclohexa-2',5'-dienylidene)]pro-panedinitrile (11d). This compound was obtained as blue crystals (acetonitrile), mp 264-266°; ir: NH_2 3425, NH 3330, 3255, CN 2220, 2215, CO 1690, C=N 1620, aryl 1600 cm^{-1}; ^1H nmr: δ 4.26 (S, 2H, CH_2), 6.28, 6.62 (d, d, 4H, C-1,2,4,5), 7.03-7.42 (m, 4H, aryl-H), 8.16 (br, 2H, NH_2), 11.05 (br, 1H, amide-NH), 11.31 (br, 1H, pyrrole-NH); ^{13}C nmr: δ 48.62 (q-C-4), 52.16 (CH_2), 64.11 (pyrrole-C-3), 73.92 (C-7'), 118.11, 119.22 (CN), 124.10, 127.53 (quino-CH), 131.96, 132.26 (aryl-CH), 128.11, 134.76 (aryl-C), 156.06 (C=N, C-5), 164.86 (C-2), 174.26 (CO), 177.42 (C-4'); ms: m/z 459/461 (M^+, 21), 395 (14), 381 (26), 331 (11), 303 (15), 261 (24), 198 (76), 118 (66), 91 (71), 77 (100), 66 (86). *Anal*. Calcd. for $C_{21}H_{14}BrN_7O$: C, 54.80; H, 3.07; Br, 17.36; N, 21.30. Found: C, 55.05; H, 2.86; Br, 17.54; N, 21.52.

2-Amino-5-(4-bromobenzyl)oxadiazole (10d). This compound was obtained as colourless crystals (ethanol), mp 185-187°; ir: NH_2 3410, C=N 1630, aryl 1595 cm^{-1}; ^1H nmr: δ 4.21 (s, 2H, CH_2), 6.88 (br, 2H, NH_2), 7.14-7.69 (m, 4H, aryl-H); ms: m/z 255/253 (M^+, 33), 211 (21), 131(36), 90 (87), 77 (100). *Anal*. Calcd. for $C_9H_8N_3BrO$: C, 42.54; H, 3.17; N, 16.54. Found: C, 42.78; H, 2.98; N, 16.29.

Acknowledgement. A. A. Hassan is indebted to the A. V. Humboldt-Foundation for the donation of the Shimadzu 408 IR spectrophotometer.

REFERENCES

[1] Chatterjee, S. *J. Chem. Soc*. **1969**, (B), 725.
[2] Rappoport, Z.; Ta-Shma, K. *J. Chem. Soc*. **1971**, (B), 1461.
[3] Fischer-Colbrie, H.; Aigner, H.; Junek, H. *Monatsh. Chem*., **1975**, *106*, 743.
[4] Rapport, Z.; Ladkani, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1045.
[5] Fatiadi, A. J. *Synthesis*, **1986**, 249, and references cited therein.
[6] Junek, H.; Klade, M.; Biza, P.; Geringer, M.; Sterk, H. *Liebigs Ann. Chem*., **1990**, 741.
[7] Junek, H.; Fischer-Colbric, H.; Hermetter, A. *Z. Naturforsch,* **1977**, *32b*, 898.
[8] Döpp, D.; J□schke, S.; Henkel, G. *Z. Naturforsch,* 2002, *57b*, 460.
[9] Hassan, A. A.; Ibrahim, Y. R.; Mohamed, N. K.; Mourad, A. E. *Liebigs Ann. Chem*., **1991**, 71.
[10] Hassan, A. A.; Mohamed, N. K.; Ibrahim, Y. R.; Mourad, A. E. *Liebigs Ann. Chem*., **1993**, 659.
[11] Hassan, A. A.; Mohamed, N. K.; El-Tamany, E. H.; Ali, B. A.; Mourad, A. E. *Monatsh. Chem*., **1995**, *126*, 653.
[12] Hassan, A. A.; Mohamed, N. K.; Aly, A. A.; Mourad, A. E. *Monatsh. Chem*., **1997**, *128*, 61.
[13] Döpp, D.; Hassan, A. A.; Nour El-Din, A. M.; Mourad, A. E.; Lehmann, C. W.; Rust, J. *Tetrahedron*, **2006**, *62*, 11618.
[14] Fatiadi, A. J. *Synthesis*, **1978**, 165.
[15] El-Saghier, A. M. M. *Phosphours, Sulfur, Silicon, Related Elements*, **2004**, *179*, 1237.
[16] Ali, A. S. E.; Afeefy, H.; Metwally, M. A. *J. Chem. Res*. **1994**, (s), 14.
[17] Abdel-Latif, F. F.; Shaker, R. M. *Bull. Chem. Soc. Fr*., **1991**, 87.
[18] Dworczak, R. *Monatsh. Chem*., **1991**, *122*, 731.
[19] Hafez, E. A.; Abdel-Galil, F. M.; Sherif, S. M.; El-Nagdi, M. H. *J. Heterocyclic Chem*., **1986**, *23*, 1375.
[20] Abdel-Latif, F. F.; Gohar, A. M. N.; Fahmy, A. M.; Badr, M. Z. A. *Bull. Chem. Soc. Jpn*., **1986**, *59*, 1235.
[21] Al-Omran, F.; El-Ghamry, I.; El-Nagdi, M. H. *Org. Prep. and Proceedures international*, **1998**, *30*, 363.
[22] Döpp, D.; Gomaa, M. A.; Henkel, H.; Nour El-Din, A. M. *J. Chem. Soc. Perkin Trans*. **1996**, II, 573.
[23] Wheland, R. C.; Martin, E. L. *J. Org. Chem*., **1975**, *40*, 3101.
[24] Martin, N.; Seoane, C. "Organic Conductive Molecules and Polymers", Nalwa (ed.). N. S.; Wiley, **1996**.
[25] Metzger, R. M.; Shumaker, R. R.; Cara, M. P.; Laidlow, R. K.; Panetta, L. A.; Torres, E. *Langmuir*, **1988**, *4*, 298.
[26] Ashwell, G. J.; Downay, E. Je.; Kuczynski, A. P.; Szablewski, M.; Sandy, I. M.; Bryce, M. R.; Grainger, A. M.; Hasan, M. *J. Chem. Soc. Faraday Trans*., **1990**, *86*, 1117.
[27] Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; R. L. Dixan, R. L.; Zhang, J. H.; Rieff, W. M.; Chittipeddi, S.; Selover, M. A.; Epstein, A. J. *J. Am. Chem. Soc*., **1990**, *112*, 5496.
[28] Zaidi, N. A.; Bryce, M. R.; Cross, G. H. *Tetrahedron Lett*., **2000**, *41*, 4645.
[29] Aly, A. A.; El-Shaieb, K. M. *Tetrahedron*, **2004**, *60*, 3797.
[30] De, S. C. *J. Indian Chem. Soc*., **1930**, *7*, 651.
[31] Henkleiss, P.; Westphal, G., Kraft, R. *Tetrahedron*, **1973**, *29*, 2937.
[32] Bansal, R. K. *J. Indian Chem. Soc*., **1989**, *59*, 277.
[33] Rivera, N. R.; Balesells, J.; Hansen, K. B. *Tetrahedron Lett*., **2006**, *47*, 4889.
[34] Ghlen, H.; Moeckel, K. *Ann*., **1962**, *651*, 133.
[35] El-Kacemi, K.; Lamache, M. *Electrochimica Acta,* **1986**, *31*, 845.
[36] El-Shaieb, K. M.; Mourad, A. E.; Hassan, A. A. *Heteroatom Chem*., **2004**, *15*, 63.
[37] Bryce, M. R.; Chinarro, E.; Green, A.; Martin, N.; Moore, A. J.; Sanchez, L.; Seoane, C. *Synthetic Metals*, **1997**, *86*, 1857.
[38] Beyer, H.; Hohn, H.; Lassig, W. *Chem. Ber*., **1952**, *85*, 1122.
[39] Wang, Z.; Shi, H. *Synthetic Comm*., **2001**, *31*, 2841.
[40] Hogyarth, E. *J. Chem. Soc*., **1949**, 1167.