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Synthesis and Properties of New Endotricyclic Electron-Rich Olefins and Their Some Derivatives

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New endotricyclic electron rich olefins (**1** and **10**) were synthesized and their new bisbenzimidazole derivatives were obtained from reaction of group 16 elements, PhNCS, CS_2 and CH_3CN. Structure of all new compounds were identified by ^1H NMR, ^{13}C NMR, FT-IR spectroscopic techniques and elemental analysis. The catalytic activity of the electron-rich olefin, **1** on the benzoin condensation reaction were also investigated.

Key Words: Electron-rich olefins, *Bis*benzimidazole derivatives, Endotricyclic compounds.

INTRODUCTION

Electron rich olefins are very reactive compounds and they are effective precursors for the preparations of variety of organic and organometallic compounds. For this reason, they have attracted considerable attention in both organic and organometallic synthetic chemistry for their unique properties[1-6].

Because of electron rich olefins are stronger π bases, they give π-complexes with many π acids and they also give transition metal complexes behave as carbene ligand[7-13]. Owing to the increased charge density on the carbon, the electron rich olefins should be oxidized much more readily than ordinary olefins and they can be used as strong reducing agents. As expected, electron rich olefins are converted into the dications by silver salts[14,15]. Electron rich olefins can be also used as an efficient catalyst for acyloin type C-C-coupling reactions[16,17].

It is known that the ultimate oxidation product of electron rich olefins with air is urea. The sulphur, selenium and tellurium reacts similarly to form the corresponding S, Se and Te analogues[18]. During the reaction of electron rich olefins with oxygen generally occur chemiluminescence. The intensity and life time of the chemiluminescence depends on the substituents at the aryl groups and or the solvent[19].

The electron rich olefins react as strong nucleophiles. They react with carbon disulfide in a molar ration of 1:2 to yield a stable dipoles. On the other hand, electron rich olefins react with proton active compounds to give products of the insertion of a nucleophilic carbene.

Although an extensive chemistry of exobicyclic electron rich olefins have long been known, but there is limited information about endotricyclic electron rich olefin contain benzimidazole moiety.

The aim of this study is to synthesize endotricyclic electron rich olefins contain benzimidazole moiety and to investigate their derivatives and compare them with those of exobicyclic electron rich olefins reported previously.

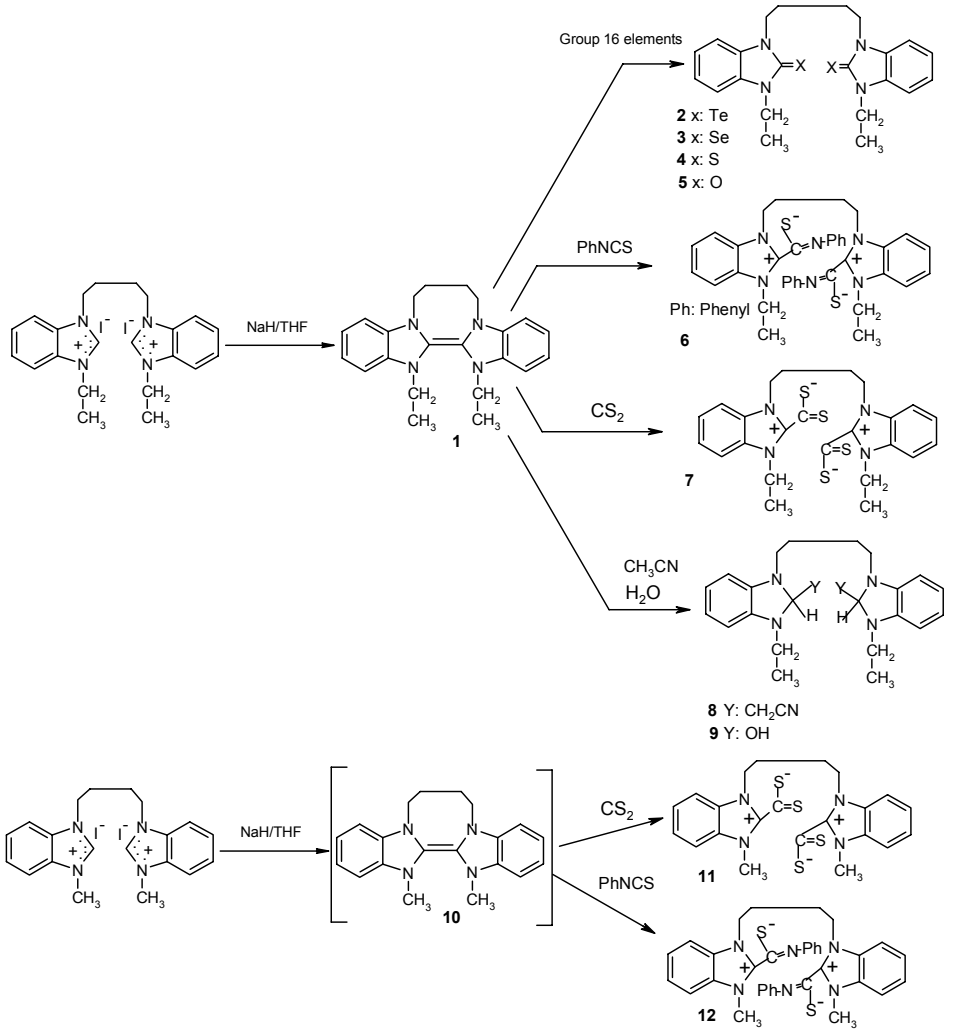
EXPERIMENTAL

All experiments were performed under the atmosphere of argon using freshly distilled dry solvents. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using Bruker DPX-300 high performance digital FT NMR (Bruker WM360, Bruker Instruments, Inc., Billerica. USA) spectrometer. Infrared spectra were recorded in the range 4000-650 cm^{-1} on an Perkin-Elmer spectrum one FT-IR spectrophotometer and samples were analyzed at ATR. Elemental analysis was performed by the elemental analysis laboratory of Inönü University Central Research Laboratory at Malatya, Turkey. Melting points were recorded using an electrothermal melting point apparatus, Electrothermal 9200 (Electrothermal Engineering Ltd., Essex, UK and are uncorrected).

General procedure: In this work, bridged benzimidazole salts were used to synthesize the corresponding electron rich olefins **1**, **10**. The compound **10** could not be crystallized and their derivatives **11** and **12** were prepared *in situ*. The olefins synthesized were converted to stable *bis*benzimidazole derivatives using appropriate reagents as summarized in **Scheme-I**.

Preparation of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane (1): A mixture of 1,4-*bis*(3-ethylbenzimidazolium)butane diiodide (8 g, 13.29 mmol) and NaH (0.6 g, 26.58 mmol) in tetrahydrofuran (THF) (50 mL) was stirred for 7 h at room temperature and the NaI separated was filtered off. The volatiles of filtrate were removed *in vacuo*. The residue was extracted with hot toluene (40 mL). The yellow coloured extract was concentrated to *ca.* 15 mL, *n*-hexane (15 mL) was added and the solution was cooled to -20 ºC to yield the compound **1**. Yield: 4.0 g, 87 %. ^{1}H NMR ($CDCl_3$): δ 1.2 (t, CH_3, 6H), 1.8 (m, -CH_2-CH_2-, 4H), 3.2-4.0 (m, -CH_2-N, 8H), 6.6-7.2 (m, Ar-H, 8H).

Preparation of 1,4-*bis*(3-ethylbenzimidazole-2-selenone-1-yl)butane (3): A mixture of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, 1, (0.7 g, 2 mmol) and selenium powder (0.36 g, 4.5 mmol) in toluene (15 mL) was heated under reflux for 2.5 h. The mixture was then filtered to remove unreacted selenium. Upon cooling the filtrate to -20 ºC the crude product was obtained. The product was crystallized from toluene/*n*-hexane mixture (2:1). Yield: 0.75 g, 75 %, m.p. 143-144 ºC. Colour: white, ^{1}H NMR ($CDCl_3$): δ 1.4 (t, CH_3, 6H), 2.0 (m, -CH_2-CH_2-, 4H), 4.4 (m, -CH_2-N, 8H), 7.2 (m, Ar-H, 8H). ^{13}C NMR ($CDCl_3$): δ 13.25, 25.32, 41.64, 46.06, 109.93, 123.30, 132.99, 165.11. FT-IR ν(C=S): 1401 cm^{-1}. Anal. calcd. for $C_{22}H_{26}N_4Se_2$: C, 52.38; H, 5.16; N, 11.11. Found: C, 51.02; H, 5.19; N, 10.34 %. Similar to compound **3**, compounds **2** and **4** were synthesized treating **1** with Te and S_8, respectively.



Scheme-I: Synthesis pathways of the new endotricyclic electron rich olefins and their derivatives

Preparation of 1,4-*bis*(3-ethylbenzimidazole-2-tellurone-1-yl)butane (2): Yield: 0.52 g, 60 %, m.p. 212-214 ºC. Colour: light green, ^{1}H NMR ($CDCl_3$): δ 1.4 (t, CH_3, 6H), 2.0 (m, -CH_2-CH_2-, 4H), 4.5 (m, -CH_2-N, 8H), 7.3 (m, Ar-H, 8H). ^{13}C NMR ($CDCl_3$): δ 13.71, 25.76, 45.09, 49.27, 111.17, 123.84, 134.07, 143.57. FT-IR $V_{C=Te}$: 1392.93 cm^{-1}. Anal. calcd. for $C_{22}H_{26}N_4Te_2$: C, 44.00; H, 4.33; N, 9.33. Found: C, 43.29; H, 4.27; N, 8.70 %.

Preparation of 1,4-*bis*(3-ethylbenzimidazole-2-thione-1-yl)butane (4): Yield: 0.5 g, 83 %, m.p. 124-126 ºC. Colour: light yellow, ^{1}H NMR ($CDCl_3$): δ 1.3 (t, CH_3, 6H), 1.9 (m, -CH_2-CH_2-, 4H), 4.3 (m, -CH_2-N, 8H), 7.2 (m, Ar-H, 8H). ^{13}C NMR ($CDCl_3$): δ 13.04, 25.19, 40.39, 44.25, 109.33, 122.89, 131.57, 168.73. FT-IR

ν(C=S): 1408 cm^{-1}. Anal. calcd. for $C_{22}H_{26}N_4S_2$: C, 64.39; H, 6.34; N, 13.66; S, 15.61. Found: C, 63.36; H, 6.61; N, 13.18; S, 16.85 %.

Preparation of 1,4-*bis*(3-ethylbenzimidazole-2-one-1-yl)butane (5): Through a solution of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, **1**, (0.6 g, 1.73 mmol) in THF (10 mL) oxygen gas was passed for 10 min. The yellow colour of **1** changed to white, while O_2 was passing through the solution. Then the volatiles were driven off and the residue was crystallized from toluene/*n*-hexane mixture (2:1). Yield: 0.69 g, 92 %, m.p. 129-130 ºC. Colour: white. ^{1}H NMR ($CDCl_3$): δ 1.2 (t, CH_3, 6H), 1.8 (m, -CH_2-CH_2-, 4H), 3.9 (m, -CH_2-N, 8H), 6.9 (m, Ar-H, 8H). ^{13}C NMR ($CDCl_3$): δ 13.67, 25.60, 35.86, 40.46, 107.74, 121.01, 129.07, 153.97. FT-IR ν(C=O): 1697 cm^{-1}. Anal. calcd. for $C_{22}H_{26}N_4O_2$: C, 69.84; H, 6.88; N, 14.82. Found: C, 68.81; H, 6.46; N, 13.54 %.

Preparation of 1,4-*bis*(3-ethyl-2-mercapto-N-phenylformimidoylbenzimidazolium-1-yl)butane inner salt (6): A mixture of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, **1**, (0.6 g, 1.73 mmol) in toluene (10 mL) was added PhNCS (0.4 mL, 3.46 mmol). The mixture was stirred at room temperature. The reaction took place shortly. All volatiles were then removed *in vacuo* and the crude product was crystallized from ethyl alcohol/DMF mixture (3:1). Yield: 0.8 g, 75 %, m.p.: 255-257 ºC. Colour: yellow, ^{1}H NMR ($CDCl_3$): δ 1.5 (t, CH_3, 6H), 2.2 (m, -CH_2-CH_2-, 4H), 4.5 (m, -CH_2-N, 8H), 7.1-7.6 (m, Ar-H, 18H). ^{13}C NMR ($CDCl_3$): δ 14.51, 26.33, 41.35, 46.42, 112.97, 122.41, 124.22, 126.55, 128.75, 129.04, 129.83, 130.43, 149.50, 151.40, 166.20. FT-IR ν(C=N): 1475 cm^{-1}. Anal. calcd. for $C_{36}H_{36}N_6S_2$: C, 70.13; H, 5.84; N, 13.64; S, 10.39. Found: C, 68.85; H, 6.18; N, 13.82; S, 11.15 %. Similarly compound **12** was synthesized from **10** and PhNCS.

Preparation of 1,4-*bis*(3-ethyl-2-dithiocarboxylatebenzimidazolium-1-yl)butane (7): A mixture of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, **1**, (0.4 g, 1.16 mmol) in toluene (10 mL) was added CS_2 (1.15 mL, 2.3 mmol). Red coloured precipitate was formed instantly. The compound was washed with diethyl ether and dried. Yield: 0.5 g, 86 %, m.p. 227-229 ºC. Colour: red, ^{1}H NMR ($CDCl_3$): δ 1.4 (t, CH_3, 6H), 1.9 (m, -CH_2-CH_2-, 4H), 4.2 (m, -CH_2-N, 8H), 7.4 (m, Ar-H, 8H). ^{13}C NMR ($CDCl_3$): δ 14.35, 26.15, 41.05, 45.08, 112.30, 112.72, 126.30, 126.57, 129.62, 130.10, 152.45, 224.10. FT-IR ν(C=S): 1050 cm^{-1}. Anal. calcd. for $C_{24}H_{26}N_4S_4$: C, 57.83; H, 5.22; N, 11.25; S, 25.70. Found: C, 56.99; H, 5.95; N, 12.39; S, 24.67 %.

Similarly compound **7** and compound **11** were synthesized from **10** and CS_2.

Preparation of 1,4-*bis*(3-ethyl-2-cyanomethylbenzimidazole-1-yl)butane (8): A mixture of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, **1**, (0.7 g, 2 mmol) in toluene (10 mL) was added CH_3CN (0.2 mL, 4 mmol) and heated and reflux for 2.5 h. All volatiles were removed *in vacuo*, the crude product obtained was crystallized from toluene/*n*-hexane mixture (2:1). Yield: 0.59, 58 %, m.p. 131-132 ºC. Colour: cream. ^{1}H NMR (DMSO-d_6): δ 1.5 (t, CH_3, 6H), 2.0 (m, -CH_2-CH_2-, 4H), 4.5 (m, -CH_2-N, 8H), 7.1 (d, CH_2CN, 4H), 7.7-8.1 (m, Ar-H, 8H), 10.0 (s, CH,

2H). ^{13}C NMR (DMSO-d_6): δ 15.22, 30.18, 45.32, 52.17, 61.05, 115.11, 130.42, 138.14, 160.02. FT-IR ν(CN): 2200 cm^{-1}. Anal. calcd. for $C_{26}H_{32}N_6$: C, 72.90; H, 7.48; N, 19.63. Found: C, 72.51, H, 7.56; N, 19.93 %.

Preparation of 1,4-bis(3-ethyl-2-hydroxybenzimidazole-1-yl)butane (9): A mixture of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, **1**, (0.6 g, 1.73 mmol) in toluene (10 mL) was added H_2O and heated and stirred at 40 ºC for 2 h. All volatiles were removed *in vacuo*, the crude product was crystallized from toluene/*n*-hexane mixture (2:1). Yield: 0.4 g, 61 %, m.p. 141-142 ºC. Colour: white, ^{1}H NMR (TFA/$CDCl_3$): δ 1.5 (t, CH_3, 6H), 2.1 (m, -CH_2-CH_2-, 4H), 4.0 (s, OH, 2H) 4.4 (m, -CH_2-N, 8H), 7.6 (m, Ar-H, 8H), 9.0 (s, CH, 2H). ^{13}C NMR (TFA/$CDCl_3$): δ 15.65, 28.23, 43.56, 50.52, 115.03, 129.19, 135.25, 157.30. FT-IR ν(C-OH): 3310 cm^{-1}. Anal. calcd. for $C_{22}H_{30}N_4O_2$: C, 69.11; H, 7.85; N, 14.66; Found: C, 68.25; H, 8.12; N, 14.65 %.

Preparation of 1,4-*bis*(3-methyl-2-dithiocarboxylatebenzimidazolium-1-yl)butane (11): Yield: 0.6 g, 86 %, m.p. 230-231 ºC. Colour: red, ^{1}H NMR (DMSO-d_6): δ 2.0 (ws, -CH_2-CH_2-, 4H), 3.9 (s, CH_3, 6H), 4.4 (ws, -CH_2-N, 4H), 7.6-8.0 (m, Ar-H, 8H). ^{13}C NMR (DMSO-d_6): δ 26.25, 32.12, 45.05, 114.16, 127.11, 130.47, 152.62, 223.13. Anal. calcd. for $C_{22}H_{22}N_4S_4$: C, 56.17; H, 4.68; N, 11.92; S, 27.23. Found: C, 55.86; H, 4.95; N, 11.83; S, 27.12 %.

Preparation of 1,4-*bis*(3-methyl-2-mercapto-N-phenylformimidoyl-benzimidazolium-1-yl)butane inner salt (12): Yield: 0.75 g, 82 %, m.p. 264-265 ºC. Colour: yellow, ^{1}H NMR (DMSO-d_6): δ 2.1 (ws, -CH_2-CH_2-, 4H), 4.0 (s, CH_3, 6H), 4.7 (ws, -CH_2-N, 4H), 7.0-8.0 (m, Ar-H, 18H). ^{13}C NMR (DMSO-d_6): δ 26.30, 32.42, 45.11, 114.08, 123.99, 127.15, 129.27, 130.02, 131.82, 150.67, 151.18, 166.53. Anal. calcd. for $C_{34}H_{32}N_6S_2$: C, 69.39; H, 5.44; N, 14.29; S, 10.88. Found: C, 69.30; H, 6.08; N, 13.95; S, 10.67 %.

Catalytic effects of 1,4-*bis*(3-ethylbenzimidazolidine-2-ylidene)butane, 1 in Benzoin condensation reaction: The compound **1** (0.02 g; 0.06 mmol) was added to a benzaldehyde (0.6 mL; 5.66 mmol) and the mixture was stirred at room temperature for 1 min. The initial orange colour of the solution was immediately discharged through exothermic reaction and within 1 min the reaction mixture had solidified. The crude product, benzoin was washed with diethyl ether and crystallized from ethanol (0.54 g, 90 %).

Similarly, 4-methylbenzaldehyde and 4-methoxybenzaldehyde were also converted to corresponding acyloin derivatives and the results obtained are given in Table-1.

RESULTS AND DISCUSSION

The structures of all the new compounds were confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis. The results obtained are given in experimental section. Related results were given at previous section. The synthesized electron rich olefins **1** and **10** and their new derivatives are shown in **Scheme-I**. The desired *bis*benzimidazole derivatives of the electron rich olefins **2-9**, **11** and **12** are air stable crystalline

TABLE-1
ACYLOIN REACTIONS CATALYZED BY ELECTRON RICH OLEFIN **1** AND THE REACTION CONDITIONS

Amount of aldehyde (mmol)	Amount of catalyst (mmol)	Temp. / Time (°C/min)	Yield (%)
Benzaldehyde			
10	0.10	20/1	90
10	0.10	100/60	82
4-Methylbenzaldehyde			
8	0.08	20/1	62
8	0.08	100/60	59
4-Methoxybenzaldehyde			
8	0.08	20/1	30
8	0.08	100/60	26

solids contrast to the starting **1** and **10** compounds which are highly sensitive. The elemental analysis and spectroscopic data are consistent with the proposed structures. Oxo, thio, seleno and telluroureas exhibit characteristic ν(C=O), ν(C=S), ν(C=Se) and ν(C=Te), bands typically at 1698-1393 cm^{-1} that compare well with 1713-1456 cm^{-1} found for the cyclic urea derived from exobicyclic ero. ^{13}C chemical shifts, which are a useful diagnostic tool for urea compounds, show that C=O, C=S, C=Se or C=Te are substantially deshilded. The values of C=O, C=S, C=Se and C=Te are 153.97, 143.57, 165.11 and 143.57, respectively and similar to those found exobicyclic electron rich olefins.

In this work, endotricyclic electron rich olefin **1** has been also tested as a catalyst for the benzoin reaction for the representative purposes. The endotricyclic olefin **1** was found to be effective catalyst for the benzoin reaction. The result was similar to the literature data obtained for the catalytic properties of the exobicyclic electron rich olefin on the benzoin reactions[16,17].

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