Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2999-3006

Preparation of Heterotricyclic Chlorides *via* Intramolecular Diels-Alder Reaction of Furans

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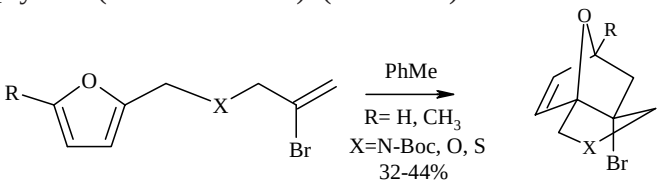
A variety of key precursors to the intramolecular Diels-Alder (IMDA) reaction of furan diene have been prepared *via* facile alkylation. Subsequently, rigid heterotricyclic chlorides **5a-e** possessing oxygen, nitrogen and sulfur have been synthesized by employing a thermal IMDA reactions. Use of bulky protecting group on nitrogen **5a-b**, such as *t*-butoxy group, can be utilized to encourage cycloaddition reactions that otherwise does not proceed.

Key Words: Intramolecular Diels-Alder, Cycloaddition, Furfurylchloroalkenes.

INTRODUCTION

Diels-Alder reactions of furan and its derivatives have received a great deal of attention because of two main reasons. Firstly, furan and some of its derivatives are inexpensive compounds obtained from agricultural by products[1]. Secondly, the cycloadducts are versatile intermediate in the preperation of carbohydrates and other biologically active compounds[2]. In addition, heteroatom in tether of furans has been found to be an internal chiral auxiliary, or ring formation for natural product synthesis[3]. However, the facile retro Diels-Alder reaction and the low reactivity of furan as a diene as a result of its aromatic character make the Diels-Alder reaction of furan one of the most difficult cycloaddition[4]. In view of these drawbacks, a range of special conditions has been developed[5]. We have been studying intramolecular reaction of furans, these heterocyclic fused tricycles, **2** include a bromo quaternary carbon centre obtained stereoselectively with moderate yields (32-44 % overall)[6] (**Scheme-I**).



1 **2**

Scheme-I

This paper describes work on cyclization of a simple N-, O-, S-substituted derivatives of furans, **4a-e** to produce the corresponding cycloadducts **5a-e**. The system **4a-e**, involving relatively an deactivated double bond adding across the aromatic furan ring, was selected since it is known to be sensitive to structural changes about the heteroatom on tether of the furan; one can utilize these compounds as a powerful strategy at the intermediate stages in a total synthesis and develop the furan chemistry.

EXPERIMENTAL

Reactions were conducted in flame dried glassware, under nitrogen atmosphere except when noted otherwise. Solvents and reagents were freshly distilled as follows: tetrahydrofuran (THF) and diethyl ether (E) were distilled from sodium/benzophenone; dichloromethane (DCM) and toluene were distilled from calcium hydride. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica plates (Macharey Nagel sil G UV_{254}). Compounds were visualized using Ultra-violet fluorescence, alkaline potassium permanganate solution or acidic cerium (IV) sulphate solution. Column chromatography was carried out Macharey Nagel Kieselgel 60 (230-240 mesh). ^1H NMR spectra were recorded on a Bruker 300 MHz DPX 300 spectrometer. The chemical shifts are quoted in ppm, as δ values downfield of tetramethylsilane (TMS) or relative to the residual solvent resonance. Infrared spectra were recorded on a Perkin-Elmer-1720 spectrophotometer; Solid samples were recorded using KBr discs and liquid samples were recorded as thin films. Elemental analysis were carried out by the microanalytisches laborataorium des institüts für Organische und Biomoleculare Chemie der Universitat Gottingen, electron ionisation mass spectra (EI, 70eV) were obtained on a Fisions VG Autospec mass spectrometer.

Synthesis of furanyl amines 4a-b

To a stirred solution of furfurylamine (**3**) (X = NH_2) (16 mmol) in THF (40 mL) was added 2,3-dichloropropene (8 mmol) and the resulting solution was heated to reflux for 12 h. A portion of potassium carbonate (5.07 g, 35.72 mmol) was then added and the reaction mixture was heated at reflux for a further 48 h. On cooling a precipitate was formed which was washed with diethyl ether (3 × 25 mL). The filtrate was extracted with 10 % NaOH (40 mL) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. To a stirred solution of resulting residue (5.35 mmol) and di-*t*-butoxy dicarbonate $(BOC)_2O$ (1.17 g, 5.35 mmol) in DCM (10 mL) was added N,N-dimethylaminopyridine (0.07 g, 0.54 mmol) at 0ºC. The reaction mixture was stirred for 2 h at ambient temperature and then concentrated under vacuum. The residue was subjected to flash column chromatography to afford the following compounds.

(2-Chloro-allyl)-furan-2-ylmethyl-carbamic acid *t*-butyl ester (4a): As colourless oil, (1.30 g, 90 %).; TLC, (hexane: ethyl acetate) (7:3), R_f : 0.73.; ν_{max} (thin film)/cm^{-1}: 2960s (C-H), 2925s (C-H), 1712s (C=O), 1172s (C-O), 726w (C-Cl); δ_H (300 MHz $CDCl_3$): 7.35 (s, 1H), 6.31 (s, 1H,), 6.24-6.18 (m, 1H), 5.31 (s, 1H), 5.26 (s, 1H), 4.47(s, 1H), 4.38 (s, 1H), 4.06 (s, 1H), 3.97 (s, 1H), 1.48 (s, 9H).; δ_C (75.5 MHz $CDCl_3$): 155.0 (q), 151.2 (q), 142.2, 138.0 (q), 112.8, 110.3, 108.0, 80.6 (q), 51.8, 42.6, 28.3 (3 × C).; m/z (GC-MS): 260 [M^+, 8 %], 203 [M^+-(*t*-Bu), 26 %], 159 [M^+-(Boc), 47 %], 185 [M^+-(C_3H_4Cl), 19 %], 81 [(C_5H_5O), 67 %].

(2-Chloro-allyl)-(5-methyl-furan-2-ylmethyl)-carbamic acid *t*-butyl ester (4b): As colourless oil, (1.40 g, 92 %).; TLC, (hexane: ethyl acetate) (7:3), R_f : 0,71.; ν_{max} (thin film)/cm^{-1}: 2957s (C-H), 2863s (C-H), 1707s (C=O), 1169s (C-O), 726w (C-Cl).; δ_H (300 MHz $CDCl_3$): 6.10-6.03 (m, 1H), 5.88-5.87 (m, 1H), 5.30 (s, 1H), 5.25 (s, 1H), 4.41 (s, 1H), 4.31 (s, 1H), 4.05 (s, 1H), 3.96 (s, 1H), 2.25 (s, 3H), 1.47 (s, 9H).; δ_C (75.5 MHz $CDCl_3$): 155.3 (q), 152.2 (q), 149.4 (q), 138.4 (q), 113.1, 109.3, 106.3, 80.7 (q), 51.9, 42.8, 28.5 (3 × C), 13.8; m/z (GC-MS): 274 [M^+, 15 %], 217 [M^+-(*t*-Bu), 32 %], 199 [M^+-(C_3H_4Cl), 21 %], 173 [M^+-(Boc), 37 %], 81 [(C_5H_5O), 52 %].

Synthesis of furanyl oxa and thioethers 4c-e

To a suspension of 0.19 g (4.8 mmol) of NaH (60 % in mineral oil) in 50 mL THF at 0°C is added 4.4 mmol of furfuryl oxa or thio alcohols **3** (X = O, S) in 5 mL THF dropwise, causing evolution of H_2 gas. After this mixture was stirred for 0.5 h at room temperature, 2,3-dichloropropene (6.6 mmol) was added. When TLC analysis showed the reaction to be complete, the mixture was re-cooled to 0°C and quenched with saturated NH_4Cl solution. The mixture was extracted with diethyl ether (3 × 50 mL). The combined extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford.

2-(2-Chloro-allyloxymethyl)furan (4c): As pale yellow oil, (0.68 g, 72 %).; TLC, (hexane: ethyl acetate) (9:1), R_f: 0.70; ν_{max} (thin film)/cm^{-1}: 2953s (C-H), 2924s (C-H), 1206s (C-O), 704w (C-Cl).; δ_H (300 MHz, $CDCl_3$): 7.44 (t, 1H), 7.27-7.17 (m, 1H), 6.37 (d, 1H, J 1.3 Hz), 5.52 (dd, 1H, J1 1.4 Hz., J2 2.9 Hz AB), 5.41 (d, 1H, J 2.9 Hz., AB), 4.52 (s, 2H), 4.01 (d, 2H, J 1.4Hz); δ_C (75.5 MHz $CDCl_3$): 153.1 (q), 145.0, 139.9 (q), 115.7, 112.3, 111.8, 74.0, 65.9.; m/z (GC-MS): 172 [M^+, 9 %], 136 [M^+-(Cl), 7 %], 98 [M^+- (C_3H_4Cl), 12 %], 81 [(C_5H_5O), 59 %].

2-(2-Chloro-allyloxymethyl)-5-methyl-furan (4d): As pale yellow oil, (0.70 g, 75 %); TLC, (hexane: ethyl acetate) (9:1), R_f : 0,75. ; ν_{max} (thin film)/cm^{-1}: 2947s (C-H), 2916s (C-H), 1118s (C-O), 714w (C-Cl); δ_H (300 MHz $CDCl_3$): 6.22(d, 1H, J 3.2), 5.87 (m, 1H), 5.46 (dd, 1H, J1 1.3 J2 2.8

AB), 5.40 (d, 1H, J 2.8, AB), 4.43 (s, 2H), 4.08 (m, 2H), 2.25 (s, 3H).; δ_C (75.5 MHz $CDCl_3$): 152.9 (q), 149.1 (q), 137.9 (q), 113.6, 111.0, 106.2, 71.8, 64.0, 13.6.; m/z (GC-MS): 186 [M^+, 6 %], 161 [M^+-(Cl), 100 %], 147 [M^+- (CH_3Cl), 20 %], 81 [(C_5H_5O), 62 %].

2-(2-Chloro-allylsulfanylmethyl)furan (4e): As pale yellow oil, (0.84 g 82 %); TLC, (hexane: ethyl acetate) (9:1), R_f: 0.77; ν_{max} (thin film)/cm^{-1} : 2961s (C-H), 2897s (C-H), 1214s (C-O), 705w (C-Cl); δ_H (300 MHz $CDCl_3$): 7.29 (dd, 1H, J1 0.7 Hz., J2 1.9Hz.), 6.25 (dd, 1H, J1 3.2 Hz., J2 1.9 Hz.), 6.11 (dd, 1H, J1 3.2 Hz., J2 0.7 Hz.), 5.30 (dd, 1H, J1 2.4 Hz., J2 1.0 Hz.), 5.27 (d, 1H, J 2.4 Hz.), 3.65 (s, 2H), 3.27 (d, 2H, J 1.0 Hz.).; δ_C (75.5 MHz $CDCl_3$): 150.9 (q), 142.3, 138.0 (q), 114.8, 110.4, 108.0, 39.1, 27.3.; m/z (GC-MS): 189 [M^+, 14 %], 161 [M^+-(O+C), 23 %], 154 [M^+-(Cl), 7 %], 113 [M^+-(C_3H_4Cl), 9 %], 81 [(C_5H_5O), 100 %].

Cycloaddition reactions of 5a-e

The oxo, mercapto and nitro-furfuryl chloroalkenes (5 mmol) was heated up to 110°C in 10 mL of toluene for 4 d at which time the reaction mixture was cooled and concentrated. Purification by column chromatography afforded the cycloadducts and in all cases, the polarity of the cycloadduct was greater that its precursor.

5-Chloro-10-oxa-3-aza-tricyclo[5.2.1.0*1,5*]dec-8-ene-3-carboxylic acid *t*-butyl ester (5a): As white solid, (0.33 g, 24 %).; m.p.: 115-117ºC.; TLC, (hexane: ethyl acetate) (7:3), R_f : 0,23; ν_{max} (thin film)/cm^{-1}: 2973s (C-H), 2933s (C-H), 1711s (C=O), 1401w (C=C), 1125s (C-O), 717w (C-Cl); δ_H (300 MHz $CDCl_3$): 6.57 (dd, 1H, J1 1.5 Hz, J2 5.8 Hz., AB), 6.48 (d, 1H, J 5.8 Hz., AB), 5.12 (dd, 1H, J1 1.5 Hz, J2 4.6 Hz.), 4.13 (d, 1H, J 12.2 Hz., AB), 4.08-4.01 (m, 1H, AB), 3.83-3.76 (m, 1H, AB), 3.55 (d, 1H, J 12.2 Hz., AB), 2.57 (dd, 1H, J1 4.6 Hz., J2 12.4 Hz., AB), 1.68 (d, 1H, J 12.4 Hz., AB), 1.48 (s, 9H); δ_C (75.5 MHz $CDCl_3$): 154.0 (q), 137.5, 133.4, 95.0 (q), 80.9 (q), 80.4 (q), 70.3, 61.7, 45.8, 41.4, 28.5 (3 × C).; m/z (GC-MS): 272 [M^+, 5 %], 252 [M^+-(CH_3 + 5H), 7 %], 241 [M^+-($2CH_3$ + H), 9 %], 216 [M^+-(*t*-Bu-H), 100 %], 172 [M^+-(Boc), 100 %]; Elemental Analysis (%): Calcd. (Found) C, 57.46 (57.68); H, 6.68 (6.74), N, 5.15 (4.98).

5-Chloro-7-methyl-10-oxa-3-aza-tricyclo[5.2.1.0*1,5*]dec-8-ene-3-carboxylic acid *t*-butyl ester (5b): As white solid, (0.31 g, 22 %), m.p.: 84-87ºC; TLC, (hexane: ethyl acetate) (7:3), R_f: 0.28; ν_{max} (thin film)/cm^{-1} : 2980s (C-H), 2932s (C-H), 1700s (C=O), 1121s (C-O), 706w (C-Cl); δ_H (300 MHz $CDCl_3$): 6.44 (d, 1H, J 5.7 Hz., AB), 6.38 (d, 1H, J 5.7 Hz., AB), 4.12 (d, 1H, J 12.1 Hz., AB), 4.01-3.94 (m, 1H, AB), 3.79-3.72 (m, 1H, AB), 3.57 (d, 1H, J 12,1 Hz., AB), 2.25 (d, 1H, J 12.5 Hz., AB), 1.79 (d, 1H, J 12,5 Hz., AB), 1.60 (s, 3H), 1.46 (s, 9H,).; δ_C (75.5 MHz $CDCl_3$):

154.3 (q), 140.8, 134.2, 96.4 (q), 80.1 (q), 74.7 (q), 61.0 (q), 48.0 (2 × C), 46.3, 28.7 (3 × C), 19.3.; m/z (GC-MS): 230 [M^+-(*t*-Bu), 8 %], 212 [M^+-(O*t*-Bu), 7 %], 186 [M^+-(Boc), 100 %], 176 [M^+-(Boc + CH_3-3H), 15 %], 148 [M^+-(Boc + CH_3 + CH_2N-3H), 18 %], 132 [M^+-(Boc + CH_3 + CH_2NCH_2-H), 11 %], 95 [(Boc-5H), 100 %]; Elemental Analysis (%): Cald. (Found) C, 58.84 (58.92); H, 7.05 (7.32); N, 4.90 (4.69).

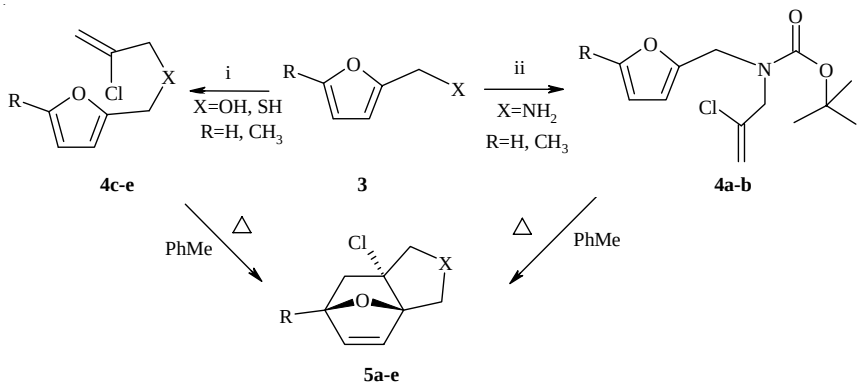
5-Chloro-3,10-dioxa-tricyclo[5.2.1.0*1,5*]dec-8-ene (5c): As colourless oil, (0.13 g, 15 %).; TLC, (hexane: ethyl acetate) (9:1), R_f: 0.28; ν_{max} (thin film)/cm^{-1}: 2944s (C-H), 2876s (C-H), 1251s (C-O), 774w (C-Cl); δ_H (300 MHz $CDCl_3$): 6.62 (dd, 1H, J1 1.6Hz., J2 5.6Hz., AB), 6.54 (d, 1H, J 5.6 Hz., AB), 5.16 (dd, 1H, J1 1.6 Hz., J2 4.6 Hz.), 4.46 (d, 1H, J 11.0 Hz., AB), 4.29 (d, 1H, J 9.8 Hz., AB), 4.16 (d, 1H, J 11.0 Hz., AB), 3.94 (d, 1H, J 9.8 Hz., AB), 2.58 (dd, 1H, J1 4.6Hz., J2 12.5Hz., AB), 1.66 (d, 1H, J 12.5 Hz., AB); δ_C (75.5 MHz $CDCl_3$): 140.4, 137.1, 89.8 (q), 80.6, 77.1, 70.8 (q), 69.2, 40.5; m/z (GC-MS): 172 [M^+, 8 %], 137 [M^+-(Cl), 3 %], 128 [M^+-(C_2H_4O), 37 %], 105 [(C_4H_6OCl), 19 %], 81 [(C_5H_5O), 80 %]; Elemental Analysis (%): Calcd. (Found) C, 55.67 (55.98); H, 5.26 (5.52).

5-Chloro-7-methyl-3,10-dioxa-tricyclo[5.2.1.0*1,5*]dec-8-ene (5d): As pale yellow oil, (0.12 g, 13 %).; TLC, (hexane: ethyl acetate) (9:1), R_f: 0.22; ν_{max} (thin film)/cm^{-1}: 2875s (C-H), 1196s (C-O), 712w (C-Cl).; δ_H (300 MHz $CDCl_3$): 6.51 (d, 1H, J 5.6 Hz., AB), 6.40 (d, 1H, J 5.6 Hz., AB), 4.40 (d, 1H, J 11.0 Hz., AB), 4.27 (d, 1H, J 9.7 Hz., AB), 4.10 (d, 1H, J 11.0 Hz., AB), 3.94 (d, 1H, J 9.7 Hz., AB), 2.24 (d, 1H, J 12.4 Hz., AB), 1.76 (d, 1H, J 12.4 Hz., AB), 1.23 (s, 3H); δ_C (75.5 MHz $CDCl_3$):138.4, 136.2, 90.6 (q), 80.6, 80.1 (q), 78.2 (q), 69.2, 46.5, 22.0.; m/z (GC-MS): 186 [M^+, 18 %], 171[M^+-(CH_3), 2 %] 151[M^+-(Cl), 42 %], 142 [M^+-(C_2H_4O), 7 %], 107 [M^+-(C_2H_4OCl), 11 %], 81 [(C_5H_5O), 79 %]; Elemental Analysis (%): Calcd. (Found) C, 57.92 (58.18); H, 5.94 (5.72).

5-Chloro-10-oxa-3-thia-tricyclo[5.2.1.0*1,5*]dec-8-ene (5e): As yellow crystals, (0.19 g, 20 %), m.p: 77-78ºC; TLC, (hexane:ethyl acetate) (9:1), R_f: 0.44; ν_{max} (thin film)/cm^{-1}: 2856s (C-H), 1218s (C-O), 720w (C-Cl); δ_H (300 MHz $CDCl_3$): 6.52 (dd, 1H, J1 1.8 Hz., J2 5.7 Hz., AB), 6.37 (d, 1H, J 5.7 Hz., AB), 5.01 (dd, 1H, J1 1.8 Hz., J2 4.8 Hz.), 3.46 (d, 1H, J 12.8 Hz., AB), 3.31 (d, 1H, J 12.2 Hz, AB), 3.21 (d, 1H, J 12.2 Hz, AB), 3.20 (d, 1H, J 12.8 Hz, AB), 2.51 (dd, 1H, J1 12.4 Hz, J2 4.8 Hz, AB), 1.74 (d, 1H, J 12.4 Hz, AB); δ_C (75.5 MHz $CDCl_3$):137.7, 135.0, 101.1 (q), 80.7, 77.7 (q), 64.5, 44.3, 29.9.; m/z (GC-MS): 189 [M^+, 5 %], 153 [M^+-(Cl), 12 %], 149 [M^+- (CH_2-C^+=CH_2), 5 %] 113 [M^+-(Cl + CH_2CH=CH_2), 10 %], 81 [(C_5H_5O), 100 %]; Elemental Analysis (%): Calcd. (Found) C, 50.93 (51.12); H, 4.81 (4.97).

RESULTS AND DISCUSSION

Furfurylchloroalkenes possessing N-, O- and S- **4a-e** were prepared *via* few facile reactions and subsequent their transformation to the IMDA cycloadducts **5a-e** was studied. Proceed of transformation underwent thermal condition by heating in toluene for 4 d. General procedure for the preparation of precursors is shown in **Scheme-II**; Oxo- and thio-furanylalkenes **4c-e** were accomplished employing Williamson ether synthesis. Treatment of furfurol and mercaptanols with sodium hydride suspension and dropwise addition of 2,3-dichloropropene gave the corresponding etheral adducts, **4c-e** in high yield. Alkylation of amines by 2,3-dichloropropene and followed by protection with *t*-butoxy (BOC) group produced the carbamides **4a-b** in high yield.



(i) NaH; 2,3-dichloropropene, THF, 2 h, 0ºC
(ii) K_2CO_3; 2,3-dichloropropene, THF, reflux, 3 d; then $(BOC)_2O$, DMAP, DCM, 0ºC, reflux for 4 d

Scheme-II

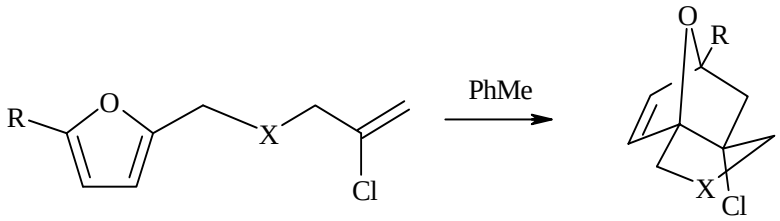
Furans, **4a-e** were subsequently refluxed in toluene (110°C) for 4 d at which time most of systems had reached their equilibrium mixtures. This thermal procedure most likely takes over facile exo transition state. Three quaternary chiral centers are generated stereogenically (R, R, S) and the chlorine atom is placed under the sterically hindered side of adducts.

Most of the products are stable and obtained as colourless solid form. Due to aromatic character of furan and vinylic chlorine, the yields given in the Table-1 belong to first cyclization are relatively low. If the recovered starting material is used repeatedly for the same transformation then yields rise up to about 70 %.

As far as the cyclization process is concerned; according to the our previous experience, if there is no heteroatom on furan's side chain then no IMDA product is observed at all. Cycloaddition for N-amines **4a-b** without protective group like Boc- or triphenyl, those behave as a steric

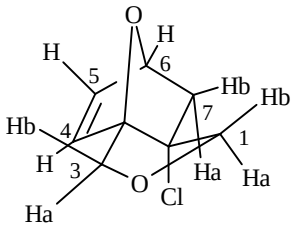
buttress and promotes the cycloaddition process does not proceed. It is observed that nitrogen linked precursors **4a-b** give higher cycloadduts than oxy- and thio-furans. Lone pair electrons of oxygen and sulphur make scissor effect (Thorpe-Ingold effect) which influence the cycloadditon process[8].

TABLE-1



Entry	**4a-e** Substrates			**5a-e** Open: Cyclic
		R	X	Yield
1	**4a**	H	*N*-$CO_2{}^t$Bu	**5a** 76:24
2	**4b**	CH_3	*N*-$CO_2{}^t$Bu	**5b** 78:22
3	**4c**	H	O	**5c** 85:15
4	**4d**	CH_3	O	**5d** 87:13
5	**4e**	H	S	**5e** 80:20

TABLE-2
NOE DATA REPRESENTS **5c**



Entry	^{1}H-^{1}H	*J* in Hz	NOE
1	6-7a	0.0	-
2	6-7b	4.5	weak
3	7a-7b	12.5	strong
4	1a-1b	10.5	strong
5	3a-3b	10.5	strong
6	3-4	-	-
7	4-5	5.6	medium

The structure and stereochemistry of the cycloadducts were determined by 2D-NMR experiments and further confirmed by X-ray crystallography.

X-ray diffraction[9] of **5e** attributed that the process is generated over facile *exo* transition state[10]. Chlorine is in *endo* position according to oxygen bridge and preferably being at sterically hindered side of the rings. The structure of newly formed ring is *exo* fused in **5c-e** and give evident from their relevant ^{1}H-^{1}H couplings (Table-2). For instance, oxygen possessed moiety **5c** can be representative of three five-membered fused systems. Thus, out of two geminal protons H-7a and 7b, only H-7b couples with H-6 (J = 4.5Hz) (Entry 2). No-coupling between H-7a and H-6 is attributable to dihedral angle of *ca.* 90° between the two protons.

Such sequential reaction offers a high degree of synthetic efficiency that they permit complex molecules to be constructed in a simple manner with great elegance and selectivity. The salient features of the strategy include high degree stereoselectivity in the cycloaddition, atom and step economy and generation of multiple chiral centers and functionalities. Further progress has been going on about to cleavage of oxygen bridge and concomitant aromatization and will be reported in due course.

ACKNOWLEDGEMENT

The authors thank The Scientific & Research Council of Turkey [TUBITAK 2377(103T121)] for financial support of this work.

REFERENCES

1. R.M. Dean, *Adv. Heterocycl. Chem.*, **30**, 169 (1982).
2. P. Vogel, J. Cossy, J. Plumet and O. Arjona, *Tetrahedron*, **55**, 13521 (1999) and references cited therein.
3. C. Andres, G. Maestro, J. Nieto, R. Pedrosa, S. Garcia-Granda and E. Perez-Carreno, *Tetrahedron Lett.*, **38**, 1463 (1997); T. J. Grinsteiner and Y. Kishi, *Tetrahedron Lett.*, **35**, 8333 (1994).
4. C.O. Cappe, S.S. Murphree and A. Padwa, *Tetrahedron*, **53**, 14179 (1997).
5. W.L. Nelson and D.R. Allen, *J. Heterocycl. Chem.*, **9**, 561 (1972); W.G. Dauben and H.O. Krabbenhoft, *J. Am. Chem. Soc.*, **98**, 1992 (1976); F. Bion, *Tetrahedron Lett.*, **23**, 5299 (1982).
6. A. Demircan and P. J. Parsons, *Synlett.*, 1215 (1998); A. Demircan and P. J. Parsons, *Heterocycl. Commun.*, **8**, 531 (2002); O. Buyukgungor, B. Kosar, A. Demircan and E. Turac, *Acta Cryst.*, **E61**, o1441 (2005); A. Demircan, M. Karaarslan and E. Turac, *Heterocycl. Commun.*, **12**, 233 (2006).
7. T.W. Greene, Protective Group in Organic Synthesis, Wiley International, New York, Ch. 7 (1981).
8. P.G. Sammes and D.J. Weller, *Synthesis*, 1205 (1995).
9. B. Kosar, E. Gokturk, C. Kazaz, O. Buyukgungor and A. Demircan, *Acta Cryst.*, **E62**, o2144 (2006).
10. R.M. Beesley, C.K. Ingold and J.F. Thorpe, *J. Chem. Soc.*, **105**, 1080, (1915); K.A. Parker and M.R. Adamchuk, *Tetrahedron Lett.*, **19**, 1689 (1978).

(*Received*: 20 July 2006; *Accepted*: 30 January 2007) AJC-5353