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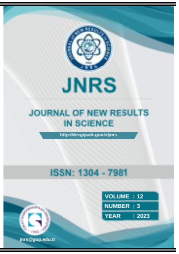

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Synthesis and trapping of spiro [bicyclo[4.2.0]octa-2,3-diene-7,2'-[1,3]dioxolane]

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Keywords:
Allene,
1,2-cyclohexadiene,
Carbene,
Doering-Moore-Skatebol reaction

Abstract — Spiro[bicyclo[3.2.0]hept-2-ene-6,2'-[1,3]dioxolane] was synthesized by the reaction of bicyclo[3.2.0]hept-2-en-6-one with ethylene glycol in yield of 92%. Addition of dichlorocarbene to Spiro[bicyclo[3.2.0]hept-2-ene-6,2'-[1,3]dioxolane] gave the 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.$0^{2,4}$]octane] in 50 % yields. Finally, the 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.$0^{2,4}$]octane] was submitted to Doering-Moore-Skatebol reaction for the synthesis of allene precursors. The reaction of the 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.$0^{2,4}$] octane] with methyl lithium (MeLi) in the presence of 1,3-diphenylisobenzofuran (DBI) as a trapping reagent under a nitrogen atmosphere at ca. 0 °C was started and continued at room temperature for four hours, resulting in the formation of four cyclo adduct isomers of spiro[bicyclo[4.2.0]octa-2,3-diene-7,2'-[1,3]dioxolane].

Subject Classification (2020): 92E10, 92E20

1. Introduction

Strained cyclic allenes, in which cumulate-double bonds are present in a ring of seven or fewer atoms, are unstable short-lived intermediates [1]. The strained and high reactivity in small ring allenes has attracted the attention of chemists and many methods have been developed for their synthesis and isolation [2]. Some of these methods are base-induced β-elimination of vinyl halides, fluroide ion-promoted elimination of β-halogenosilane and Doering-Moore-Skatebol reaction [3-5]. The first studies on the synthesis of strained allenes were carried out in the 1935s. Later, Ball and Landor [6] reported that they synthesized 1,2-cycloheptadiene and 1,2-cyclootadiene. Conclusive evidence for the formation of 1,2-cyclohexadiene was reported by Wittig and Fritze in 1968 [7]. Moore and Moser synthesized 1,2-cyclohexadiene using the carbenoid method [8]. Balcı and Jones isolated the optically active cycloaddition products of 1,2-cyclohexadiene [9].

In our studies for the synthesis of strained allenes [10-12], 1,2-cyclohexadiene was obtained by fluoride ion supported β-halogenosilane elimination [5]. In addition, 1-phenyl-1,2-cyclohexadiene and -heptadiene were successfully synthesized by the base-induced HI-elimination reaction [13,14]. Moreover, the first evidence of the formation of 1,2-cyclopetaidene was reported by our group [15]. In recent years, the synthesis, trapping, and theoretical study of strained cyclic allenes have again become a focus of increasing interest. West et al. synthesized keto-substituted 1,2-cyclohexadiene and trapped them with various furan-based 1,3-dienes or enamine dienophiles [16,17].

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In other study, the trapping products of 1,2-cyclohexadine with 1,3-diphenylisobenzofuran were isolated from treated with tetrabutylammonium fluoride (TBAF) and α-bromo enol triflate cyclohexene by Okano et al [18,19]. Additionally, Garg et al. theoretically examined the mechanism of the trapping products of 1,2-cyclohexadiene and suggested that the mechanism proceeds through the monoracial intermediate [20]. In this study, the synthesis of spiro[bicyclo[4.2.0]octane-7,2'-[1,3]dioxolane]-2,3-diene (**14**), a derivative of 1,2-cyclohexadiene, was carried out by carbenoid method.

2. Experimental Section

2.1. Material and Methods

All synthesized and application reagents were purchased (from Sigma-Aldrich Chemical) commercially and did not require further purification. IR spectrums (KBr/KCl or liquid) were taken by a Jasco FT-IR-430 IR spectrophotometer in the range 4000-650 cm^{-1}. ^1H-NMR and ^{13}C-NMR spectra were recorded on a Brucker Advance III device (400 and 100 MHz). As internal standards served TMS (δ 0.00) for ^1H-NMR and $CDCl_3$ (δ 77.0) for ^{13}C-NMR spectroscopy J values are given in Hz. 's' (singlet), 'd' (doublet), 't' (triplet), 'm' (multiplet), 'br.' (broad) and combinations thereof are used to denote the multiplicities of the signals in the ^1H-NMR spectra. Column chromatography using Al_2O_3 column (100 g, active basic-III) was utilized to isolate the products.

2.2. Addition of Dichlorocarbene to Bicyclo[3.2.0]hept-2-en-6-one (5)

To suspension of potassium-*tert*-butoxide 1.04 g (9.3 mmol) in dry petroleum ether (15 mL) at ca. 0 °C was added bicyclo[3.2.0]hept-2-en-6-one (**5**) 1.0 g (9.3 mmol). To magnetically stirring solution was added $CHCl_3$ (7.6 g, 65 mmol) for 1 hour and stirred at room temperature for 17 hours. The reaction mixture was poured to finely crushed ice and extracted with diethyl ether (2 x 50 mL). The organic layer was dried over Na_2SO_4, and solvent was removed in vacuum. The products, 2,2-dichloro-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**6**) and 3,3-dichloro-3,3a,4,6a-tetrahydropentalen-2(1*H*)-one (**7**), were isolated as the mixture in yield of 60 % (1.1 g). ^1H-NMR (400 MHz, $CDCl_3$, ppm): δ= 5.78-5.56 (m, 4H), 3.87-3.51 (m, 3H), 3.48-3.06 (m, 3H), 2.66-2.38 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 200.0, 198.7, 136.4, 133.2, 132.8, 132.3, 78.9, 74.6, 49.4 (2C), 45.4, 40.4, 40.2 (2C), 34.9, 32.9; IR (KCl, cm^{-1}): 2946, 2873, 1639, 1446, 1032, 810, 757.

2.3. Synthesis of Spiro[bicyclo[3.2.0]hept-2-ene-6,2'-[1,3]dioxolane] (8)

To solution of bicyclo[3.2.0]hept-2-en-6-one (**5**) 3.0 g (30 mmol) in benzene (100 mL) was added ethylene glycol (11.16 g, 180 mmol) and catalytic amount of *p*-TsOH. The reaction mixture was refluxed with Dean-Strak apparatus for 5 hours. The mixture was cooled to room temperature and washed with saturated solution of $NaHCO_3$ and water. The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuum. The crude product was purified on Al_2O_3 column (active basic–III) eluting with petroleum ether/diethyl ether (98:2). Spiro[bicyclo[3.2.0]hept-2-ene-6,2'-[1,3]dioxolane] (**8**) was obtained as a viscous liquid in yield of 92 % (3.89 g). ^1H-NMR (400 MHz, $CDCl_3$, ppm): δ= 5.81-5.69 (m, 2H), 4.08-3.89 (m, 4H), 3.49-3.38 (m, 1H), 3.26-3.08 (m, 1H), 2.94-2.72 (m, 2H), 2.29-1.98 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 135.3, 129.5, 104.3, 64.1, 63.9, 43.2, 40.6, 38.4, 34.1; IR (KCl, cm^{-1}): 2935, 2884, 1652, 1558, 1455, 1079, 1031, 765.

2.4. Synthesis of 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.0^{2,4}]octane] (9)

To suspension of potassium-*tert*-butoxide 7.3 g (65 mmol) in dry petroleum ether (50 mL) at ca. 0 °C was added spiro[bicyclo[3.2.0]hept-2-ene-6,2'-[1,3]dioxolane] (**8**) 1.0 g (6.5 mmol). To magnetically stirring solution was added $CHCl_3$ (7.6 g, 65 mmol) in 15 mL of petroleum ether for 1 hour and stirring at room temperature for 17 hours. The reaction mixture was poured to finely crushed ice and extracted with petroleum ether (2 x 50 mL). The organic layer was dried over Na_2SO_4, and solvent was removed in vacuum. The crude product was purified on Al_2O_3 (20 g) column (active basic –III) eluting with petroleum ether/diethyl ether (8:2). 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.0^{2,4}]octane] (**9**) was obtained as a viscous liquid in yield of 50 % (0.77 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ= 3.85-3.67 (m, 4H), 2,77-2.67 (m, 1H), 2.61 (dd, *J*= 11.0, 7.2 Hz, 1H), 2.43 (ddd, *J*= 13.5, 8.7, 3.5 Hz, 1H), 2.37 (ddd, *J*= 14.0, 6.4, 3.4 Hz, 1H), 2.18 (dt, *J*= 6.8, 0.6 Hz, 1H), 2.04 (dd, *J*= 13.5, 5.6 Hz, 1H), 2.02-1.88 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 105.8, 67.4, 64.3, 63.4, 53.8, 42.6, 39.0, 37.8, 34.5, 28.3; IR (KCl, cm^{-1}): 2937, 2884, 1448, 1423, 1020, 789.

2.5. Reaction of 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.0^{2,4}]octane] (9) with $AgNO_3$ or $AgClO_4$

To mixture of 3',3'-dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.0^{2,4}]octane] (**9**) (0.4 g, 1.7 mmol), 9 mL of acetone and 1 mL of H_2O was added $AgNO_3$ (0.29 g, 1.7 mmol). The reaction mixture was heated at 180 °C (oil bath temperature) for 4 hours. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. To residue was added diethyl ether and washed with water. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. The crude product was purified on a silica gel column eluting with $CHCl_3$/diethyl ether (1:1). 3,3-Dichlorotricyclo [4.2.0.0^{2,4}]octan-7-one (**4**) was obtained as a viscous liquid in yield of 40 % (0.13 g). The above reaction was repeated with $AgClO_4$ instead of $AgNO_3$ and 3,3-dichlorotricyclo[4.2.0.0^{2,4}]octan-7-one (**4**) was obtained in yield of 53 % (0.17 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ= 3.41 (m, 1H), 3.04 (m, 1H), 3.25-3.17 (ddd, *J*= 18.1, 9.3, 4.2 Hz, 1H), 2.82-2.75 (ddd, *J*= 18.1, 4.7, 3.2 Hz, 1H), 2.52-2.39 (ddd, *J*= 15.7, 6.3, 2.9 Hz, 1H), 2.18-2.01 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 204.8, 66.5, 58.4, 45.8, 36.3, 34.7, 29.8, 28.6; IR (KCl, cm^{-1}): 2919, 2852, 1641, 1452, 1180, 889, 645.

2.6. Reaction of 3',3'-Dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.0^{2,4}]octane] (9) with MeLi

To mixture of 3',3'-dichlorospiro[1,3-dioxolane-2,7'-tricyclo[4.2.0.0^{2,4}]-octane] (**9**) (0.36 g, 1.53 mmol) and DBI (0.42 g, 1.53 mmol) in dry THF (2 mL) under N_2 atmosphere at ca. 0 °C was added MeLi (1.9 mL, 1.53 mmol) dropwise. And the mixture was stirred at room temperature for 4 hours. H_2O (5 mL) was added to reaction mixture and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was submitted to Al_2O_3 column (100 g, active basic-III) for separating the products. The petroleum ether/diethyl ether (85:15) was used as eluting solvent.

First fraction (exo-izomer): (4'R,9'R,9a'S)-4',9'-diphenyl-2a',4',9',9a',10',10a'-hexahydro-2'H-spiro [[1,3]dioxo- lane-2,1'-[4,9]epoxycyclobuta[b]anthracene] (15b)

Yield of 7.2% (48 mg). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ= 7.79-7.72 (m, 2H), 7.58-7.53 (m, 6H), 7.45-7.41 (m, 4H), 7.18-7.14 m, 2H), 5.97 (dd, *J*= 6.8, 2.2, Hz, 1H), 3.89-3.81 (m, 4H), 3.02-2.97 (dq, *J*= 12.4, 4.6 Hz, 1H), 2.75-2.65 (m, 2H), 2.30-2.23 (m, 1H), 1.94-1.86 (m, 2H), 0.83-0.75 (dq, *J*=12.7, 6.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 145,1, 145.0, 137.0, 136.0, 128.5, 128.4, 128.3, 127.5, 127.2, 127.1, 126.7, 125.9, 125.7, 121.3, 119.6, 118.6, 107.5, 89.5, 89.4, 64.8, 64.3, 45.7, 44.1, 43.9, 25.2, 23.5; IR (KBr, cm^{-1}): 2919, 2852, 1641, 1452, 1180, 889, 645. Analytically calculated for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.96; H, 6.23.

Second fraction (endo-isomer): (4'R,9'R,9a'R)-4',9'-diphenyl-2a',4',9',9a',10',10a'-hexahydro-2'H-spiro [[1,3] dioxolane-2,1'-[4,9]epoxycyclobuta[b]anthracene] (15a)

Yield of 31.2% (0.21 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ= 7.82-7.77 (m, 4H), 7.51-7.45 (m, 8H), 7.32-7.27 (m, 2H), 5.85 (dt as p, *J*= 3.7, 2.8, Hz, 1H), 3.89-3.74 (m, 4H), 3.19 (d, *J*= 5.9 Hz, 1H), 2.89-2.83 (m, 1H), 2.63-2.61 (dd, *J*= 5.9, 4.6 Hz, 1H), 2.58 (t, *J*= 5.9 Hz, 1H), 2.20-2.15 (q, *J*= 6.9 Hz, 1H), 2.13-2.05 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 148.5, 146.6, 135.4, 133.7, 129.2, 129.1, 128.5, 128.4, 128.3, 128.2, 127.1, 126.6, 126.5, 126.3, 122.8, 120.5, 106,5, 90,5, 88.2, 64.2, 63.4, 54.0, 53.5, 40.2, 37.6, 26.8; KBr, cm^{-1}): 2930, 2863, 1651, 1458, 11190, 879, 648. Analytically calculated for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.88; H, 5.98.

Third fraction (exo-isomer): (5'S,10'S,10a'R)-5',10'-diphenyl-2a',3',5',10',10a',10b'-hexahydro-1'H-spiro[[1,3] dioxolane-2,2'-[5,10]epoxycyclobuta[a]anthracene] (16b)

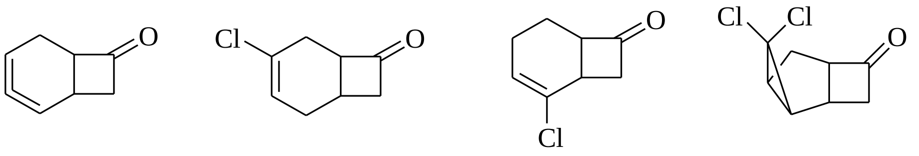
Yield of 4.8% (26.1 mg). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ= 7.86 (brd, J = 7.1 Hz, 1H), 7.72 (brd, J = 7.1 Hz, 1H), 7.51-7.39 (m, 8H), 7.27-7.13 (m, 4H), 5.71 (t, *J*= 2.4, Hz, 1H), 3.89-3.85 (m, 2H), 3.81-3.73 (m, 2H), 2.96-2.93 (dt, *J*= 8.6, 4.0 Hz, 1H), 2.76-2.65 (m, 2H), 2.34-2.22 (m, 2H), 1.71-1.66 (dd, *J*= 12.1, 8.4 Hz, 1H), 0.68-0.59 (q, *J*= 12.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 147.3, 145.9, 144.8, 138.2, 135.3, 128.7, 128.6, 128.5, 128.4, 128.3, 127.5, 127.1, 126.5, 121.8, 121.6, 118.4, 107.0, 90.3, 90.1, 64.6, 63.5, 46.6, 45.9, 40.9, 26.7, 26.4; IR (KBr, cm^{-1}): 2926, 2848, 1647, 1458, 1185, 882, 650. Analytically calculated for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.12; H, 6.13.

Forth fraction (endo-isomer): (5'S,10'S,10a'S)-5',10'-diphenyl-2a',3',5',10',10a',10b'-hexahydro-1'H-spiro [[1,3]dioxolane-2,2'-[5,10]epoxycyclobuta[a]anthracene] (16a)

Yield of 24% (0.16 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ= 7.89-7.86 (m, 4H), 7.57-7.21 (m, 8H), 7.19-7.19 (m, 4H), 6.04 (dd, *J*= 5.9, 2.5 Hz, 1H), 3.98-3.76 (m, 4H), 2.98 (d, *J*= 7.7 Hz, 1H), 2.88-2.83 (m, 1H), 2.75-2.2.66 (m, 1H), 2.46 (dd, *J*= 16.1, 8.4 Hz, 1H), 2.13 (t, *J*= 7.7 Hz, 1H), 0.33-0.26 (dq, *J*= 12.5, 7.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 148.2, 146.4, 145.2, 138.3, 136.1, 129.6, 129.1, 128.9, 128.5, 128.3, 127.8, 127.3, 126.9, 122.4, 121.8, 118.7, 107.2, 90.8, 90.2, 64.8, 63.7, 46.9, 45.9, 41.1, 27.8, 26.9; IR (KBr, cm^{-1}): 2934, 2861, 1655, 1449, 1179, 891, 641. Analytically calculated for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.94; H, 6.08.

3. Results and Discussions

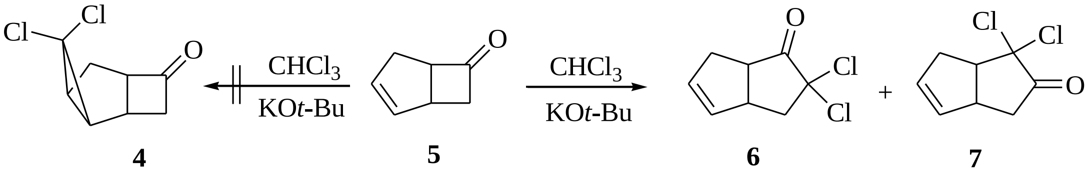
By our approach, we envisaged that β-elimination from **2** and **3** and Doering-Moore-Skatebol reaction of **4** could give allene **1**. Bicyclo[3.2.0]hept-2-en-6-one (**5**) was used as a starting material to synthesis of the allene precursor compounds **2**, **3,** and **4** (Figure 1).



1 **2** **3** **4**

Figure 1. Allene precursor

Addition of dichlorocarbene to bicyclo[3.2.0]hept-2-en-6-one (**5**) gave the two ring expansion products, 2,2-dichloro-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**6**) and 3,3-dichloro-3,3a,4,6atetrahydropentalen-2(1*H*)-one (**7**) (Scheme 1), in spite of expected addition product 3,3-dichlorotricyclo [4.2.0.0^{2,4}] octan-7-one (**4**). Despite all the attempts chromatographically, the products **6** and **7** were not separated.

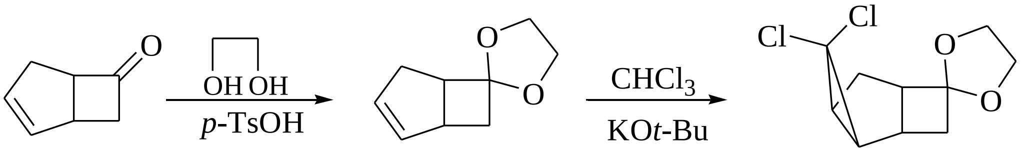


4 **5** **6** **7**

Scheme 1. Addition of dichlorocarbene to bicyclo[3.2.0]hept-2-en-6-one (5)

The structures of compounds **6** and **7** were determined ^{1}H- and ^{13}C-NMR studies of the mixture. In the ^{13}C-NMR spectrum of the mixture, 16 lines were observed as expected. The two carbonyl signals (at δ 200.0 and 198.7), four olefinic signals (at δ 136.4, 133.2, 132.8, and 132.3), two $\underline{C}$-Cl signals (at δ 78.9 and 74.6) and eight signals in the aliphatic region indicate the proposed structures **6** and **7**.

The carbonyl group was protected with ethylene glycol to add dichlorocarbene to double bond. The refluxing of **5** with ethylene glycol in the presence of *p*-TsOH (*para*-toluene sulfonic acid) under azeotropic conditions in benzene for 4 hours afforded the ketal **8** in 92 % yields (Scheme 2). The compound **8** was purified by Al_2O_3 column eluting petroleum ether/diethyl ether (98/2). Disappearing of the carbonyl signal and appearing three etheric carbon signals (at δ 104.3, 64.1, and 63.99, respectively) in the ^{13}C-NMR spectrum of compound **8** confirm the structure **8**.



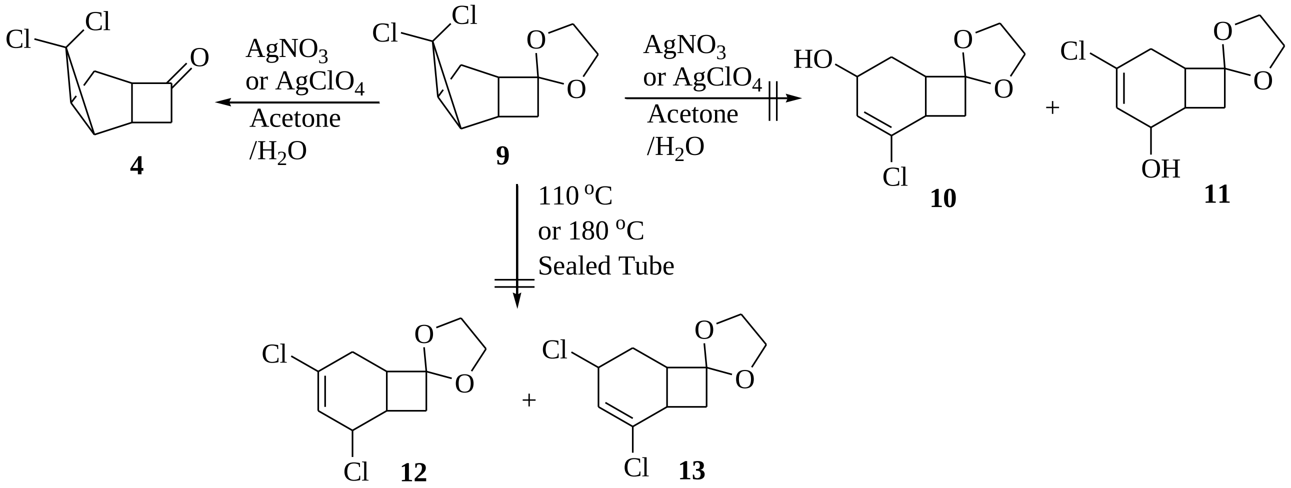
5 **8** **9**

Scheme 2. Protection of **5** and carbene addition to **8**

The treatment of compound **8** with $CHCl_3$ and KO*t*-Bu in petroleum ether at room temperature for 17 hours resulted in the formation of dichlorocarben adduct **9** in 50 % yields (Scheme 2). The compound **9** was purified by Al_2O_3 column eluting petroleum ether/diethyl ether (98/2). The structure of **9** was determined based on spectral data. Disappearing of the olefinic carbon signals, appearing a new carbon signal arising from -CCl_2 carbon (at δ 67.4 and total ten signals in the ^{13}C-NMR spectrum indicate the expected structure **9**.

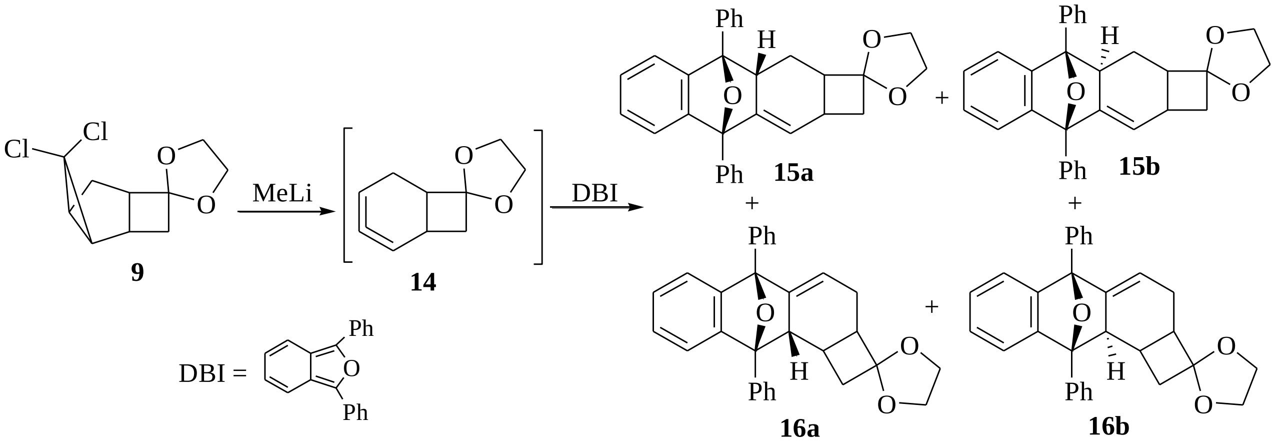
We think that the thermal rearrangement of **9** gives ring opening products **12** and **13** followed by reduction of allylic chlorine atom with $LiAlH_4$ gives the allene precursors **2** and **3**. For this purpose the compound **9** was heated in CCl_4 at 110 °C (oil bath temperature) for 18 hours but did not any transformation. The heating was repeated in sealed tube at 180 °C (oil bath temperature), also in this case, no change was not observed.

Therefore, compound **9** was submitted to silver ion supported ring opening reaction to obtain compounds **10** and/or **11** having allyl hydroxyl group which can convert to dichloro compounds **12** and **13** with PCl_3 followed by reduction give the compounds **2** and **3**. The treatment of **9** with silver nitrate ($AgNO_3$) in acetone/H_2O (9/1) at room temperature did not have any reaction. But, refluxing of the mixture gave the hydrolyzed compound **4** in 40 % yields instead of expected **10** and/or **11**. The reaction was repeated the same conditions using $AgClO_4$ instead of $AgNO_3$, in this case the hydrolyzed compound **4** was obtained in 53 % yields (Scheme 3). The structure of compound **4** was determined by spectroscopic methods. The disappearance of the bridge -CH_2CH_2- signals in the ^{1}H-NMR spectrum and the observation of the -CCl_2 carbon signal in the ^{13}C-NMR spectrum confirm the structure.



Scheme 3. Rearrangement reactions of **9**

Finally, compound **9** was submitted to Doering-Moore-Skatebol reaction for the synthesis of allene **1**. The reaction of **9** with MeLi in THF in the presence of DBI (1,3-diphenylisobenzofuran) as a trapping reagent under nitrogen atmosphere was started at ca. 0 °C and continued at room temperature for 4 hours. In the ^{1}H-NMR spectrum of the crude product, observing four separately signals (at δ6.04, 5.97, 5.85 and 5.71 ppm) in the olefinic region indicate the formed four allene cycloadducts (**15a,b** and **16a,b**) in total yields of 63.2% (Scheme 4). The ratio of products was determined as 5:6.5:1.5:1, respectively, from the integral values of olefinic protons signals. The isomers were separated by column chromatography (Al_2O_3 column (100 g, active basic-III)) eluting with petroleum ether/diethyl ether (85:15).



Scheme 4. Synthesis of allene trapping products **15a,b** and **16a,b**

The structures of isomers were explained by NMR studies and literatures data [5, 12, 13]. The four signal groups (at δ5.97, 5.85, 5.71 and 6.04 ppm) observed in the olefinic region in the NMR spectrum clearly indicate that the four isomers are formed. Moreover, according to the literature information, the bridge -CH proton of the endo isomers resonates in the low field, while that of the exo isomer resonates in the up field. The -CH protons of endo isomers of **15b**, **16b** resonate at d 3.19, 2.98 ppm, while those of exo isomers of **15a**, **16a** resonate at d 2.98, 2.94 ppm, respectively.

4. Conclusion

In this study, the addition of dichlorocarbene to bicyclo[3.2.0]hept-2-en-6-one (**5**) and rearrangements of adduct were investigated. The addition of dichlorocarbene to bicyclo[3.2.0]hept-2-en-6-one (**5**) gave the two ring expansion reaction instead of expected addition reaction to double bond. After the carbonyl group in **5** was protected with ethylene glycol, dichlorocarbene added to double bond and the dichlorocarbene adduct **9** was obtained in 50% yields. Compound **9** was submitted to the thermal rearrangement reaction at 110 °C and 180 °C for the synthesis of allene precursors **2** and **3** but did not any transformation. Addition, to obtained allene precursors **2** and **3**, compound **9** treated with silver nitrate ($AgNO_3$) and silver perchlorate ($AgClO_4$), separately, and the gave the hydrolyzed product **4.** Finally, compound **9** was submitted to Doering-Moore-Skatebol reaction for the synthesis of allene **1**. The reaction of **9** with MeLi in the presence of DBI (1,3-diphenylisobenzofuran) as a trapping reagent and four cycloadducts were obtained in total yield of 63.2%. We can say that this method can be used in the synthesis of strained cyclic allenes with face-to-face ring systems containing carbonyl groups.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflict of Interest

All the authors declare no conflict of interest.

Supplementary Material

https://dergipark.org.tr/en/download/journal-file/29054

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