Article

JOURNAL OF THE CHINESE CHEMICAL SOCIETY

Some Reactions of *gem*-Dibromocyclopropanes and Metal Carbonyls

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(Received Jun. 18, 2011; Accepted Oct. 13, 2011; Published Online Oct. 27, 2011; DOI: 10.1002/jccs.201100375)

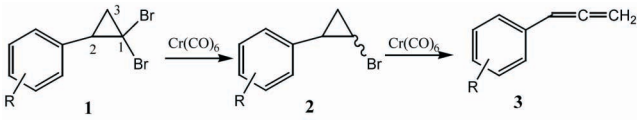
A series of *gem*-dibromocyclopropanes were treated with various metal complexes. Among the metal complexes, $Ru(CO)_2(PPh_3)_3$, $Ru(CO)_3(PPh_3)_2$, and $Mo(CO)_6$ were able to remove a bromine atom from 1,1-dibromo-2-phenylcyclopropanes (**1**) to yield a series of corresponding of 1-bromo-2-phenylcyclopropanes (**2**). Upon the treatment of **1** with $Cr(CO)_6$ in DMSO, a series of allenes were obtained in good yields. The correlation between the rate of formation of allenes and the substituents on the benzene gives a negative coefficient which suggests the dibromocyclopropanes possesses as an electrophile toward to $Cr(CO)_6$. In the presence of $Cr(CO)_6$, *gem*-dibromobicyclo[n,1,0]alkanes (**4**) in DMF or DMSO solution underwent the cleavage of carbon-bromine bond followed by ring-expansion and coupling reaction to form bicycloalkenes **7**.

Keywords: *gem*-Dibromocyclopropane; Chromium carbonyl; Debromination; Ring-opening; Coupling.

INTRODUCTION

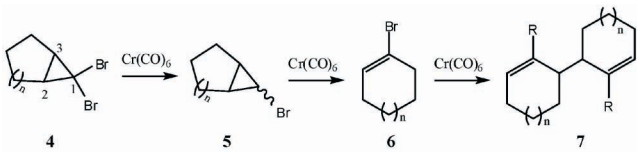
The structure of cyclopropane ring possesses a high ring strain character. With additional halogen, *gem*-dihalocyclopropanes have played an important role in organic synthesis.[1] They are valuable substrates for the preparation of monohalocyclopropanes, cyclopropanes, cyclopropenes, allenes, and many other hydrocarbon systems.[2] For example, the versatile chemical intermediate 1,3,5-cyclohepatriene has been prepared by thermal rearrangement of 7,7-dihalonorcaranes.[3] Due to their exceptional availability, the intensive studies on their chemistry have been carried out. Aryldihalocyclopropanes were converted to allenes in the presence of strong bases, such as MeLi[4], $CrCl_3/LiAlH_4$,[4] SmI_2[5] and Grignard reagent.[6] On the fused *gem*-dihalobicyclo[n.1.0]alkane, the ring expansion was easily undergoing by treatment of silver-ion[7] or under high temperature condition.[8] Low valence metals are readily used to undergo insertion into the carbon-halogen bond for coupling reaction or reduction.[9] To our best knowledge, reaction of metal carbonyl and dibromocyclopropane has not been described. Herein, we report the formation of allenes and ring-expansion-coupling products from the treatment of arylcyclopropane (Scheme I) and fused cyclopropanes (Scheme II) with $Cr(CO)_6$, respectively. Since $Cr(CO)_6$ is a commercially available, stable in air and inexpensive reagent, it can be useful for many synthetic methods.

Scheme I



R = H (**a**), 3-CH_3 (**b**), 4-CH_3 (**c**), 3-OCH_3 (**d**), 4-OCH_3 (**e**), 3-Br (**f**), 4-Br (**g**), 3-Cl (**h**), 4-Cl (**i**)

Scheme II



n = 1 (**a**) R = Br;
n = 2 (**b**), 3 (**c**), 4 (**d**) R = H

RESULTS AND DISCUSSION

In continuing our effort on seeking the application of cyclopropanes, we used the various lower valence metallic complexes to activate the 1,1-dibromo-2-phenylcylopropane (**1a**) and determined the final transformation products. The progress of reaction was monitored by using GC/MS analysis and the results were summarized in Table 1. Among the used metallic complexes, $RuCl_2(PPh_3)_3$, $W(CO)_6$, and $Co_2(CO)_8$ (entries 1~3, 8, 9) in the used solvents were inert; $Ru(CO)_2(PPh_3)_3$, $Ru(CO)_3(PPh_3)_2$ and $Mo(CO)_6$ (entries 4~7, 10) yielded 1-bromo-2-phenylcy-

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Table 1. Reaction of 1,1-dibromo-2-phenylcyclopropane with various metallic complexes

Entry	Metallic complex	Solvent	Temp.(°C)/time	Product[a]
1	$RuCl_2(PPh_3)_3$	*i*-PrOH	reflux/3 days	no reaction
2	$RuCl_2(PPh_3)_3$	CH_3CN	reflux/3 days	no reaction
3	$RuCl_2(PPh_3)_3$	DMSO	130 °C/1 day	**2a** (trace)
4	$Ru(CO)_2(PPh_3)_3$	CH_3CN	reflux/1 day	**2a** (14%)
5	$Ru(CO)_2(PPh_3)_3$	C_6H_{12}	reflux/3 h	**2a** (81%)
6	$Ru(CO)_2(PPh_3)_3$	DMSO	130 °C/12 h	**2a** (90%)
7	$Ru(CO)_3(PPh_3)_2$	CH_3CN	reflux/3 days	**2a** (10%)
8	$W(CO)_6$	DMSO	130 °C/12 h	no reaction
9	$Co_2(CO)_8$	DMSO	130 °C/12 h	no reaction
10	$Mo(CO)_6$	DMSO	130 °C/12 h	**2a** (20%)
11	$Cr(CO)_6$	DMSO	130 °C/0.5 h	**2a** (15%) + **3a** (53%)
12	$Cr(CO)_6$	DMSO	130 °C/2 h	**3a** (86%)
13	$Cr(CO)_6$	DMSO[b]	130 °C/2 h	**2a** (18%) + **3a** (26%)
14	$Cr(CO)_6$	DMF	130 °C/12 h	**3a** (81%)
15	$Cr(CO)_6$	DMSO[c]	130 °C/6 h	**2a** (32%)

Reactions of dibromocyclopropane **1a** (1.0 mmol) and metallic complex (1.0 mmol) in used solvent (10.0 mL) was carried out at indicated condition.
[a] Yields were measured based on the area ratio from crude products by GC/MS analysis.
[b] 0.5 mmol of $Cr(CO)_6$ was used.
[c] 1,1-Dichloro-2-phenylcyclopropane was used as reactant.

clopropane (**2a**). Compound **2a** were verified by comparing the retention time from GC analysis and the mass spectra with the authentic compound obtained from reduction of corresponding dibromocyclopropane **1a** using diethyl phosphate and triethylamine.[10] **1a** was converted into allene **3a** by treatment of $Cr(CO)_6$ in DMSO solution in good yield (entries 11, 12). If DMF is used instead of DMSO, longer reaction time is required to obtain the comparable result (entry 14). Half of equivalent amount of $Cr(CO)_6$ only converts partial of **1a** into allene (entry 13). Equivalent amount of $Cr(CO)_6$ was necessary to remove two bromine atoms from cyclopropane ring for the further reaction. The *gem*-dichloro counterpart (entry 15) only underwent reduction with substantial slow reaction rate. Higher polar aprotic solvent was required for the debromination and formation of allene. The formation of green precipitates indicated the conversion of Cr(0) into stable Cr(III) species.

The carbene has been proposed as an intermediate for the transformation of dihalocyclopropanes into allene.[11] We attempted to use cyclohexene as a trapping agent in the mixture of compound **1a** and $Cr(CO)_6$. After work-up, none of bicyclo[4,1.0]heptane adduct was detected except allene **3a**. The result implied that the formation of allene **3a** from monobromocyclopropane **2a** was a rapid process and no free carbene was detected.

To determine the progress of reaction, the composition of products were monitored by using GC/MS analysis and the identities of products were verified by analysis of their mass spectra. The concentrations of product on various reaction times are depicted at Fig. 1. From the figure, we find that the allene is formed right after the formation of monobromocyclopropane **2a** and its concentration is higher than that of **2a** along the progress of reaction. That

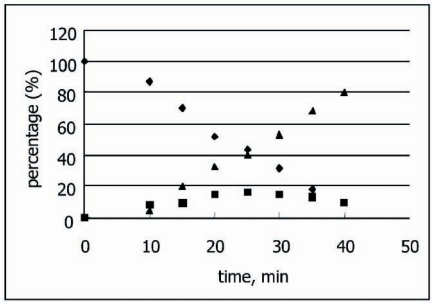

Fig. 1. Concentration of **2a** and **3a** with time during the reaction of **1a** and $Cr(CO)_6$ at 130 °C. ◆: 1,1-dibromo-2-phenylcyclopropane (**1a**), ■: 1-bromo-2-phenylcyclopropane (**2a**), ▲: 1,2-Propadienylbenzene (**3a**). The amounts (yields) of **1a**, **2a**, and **3a** were estimated based on the areas determined by GC-MS analysis.

might indicate the rate determining step is the removal of first bromine atom and the removal of second bromine along with allene formation is a fast process. The maximum amount of **2a** appears at 25 min.

During the reaction between low valence metal and carbon-bromine bond, the metal undergoes an oxidative-addition process (insertion process).[12] The electron density of carbon-bromine bond would influence on the rate of insertion and/or further process. The substituent on the phenyl ring can affect the electron-density of the cyclopropane ring. Hammett's equation is used to demonstrate the intense of effect on the reaction rate by substituent. In this work, the competition reactions between 1,1-dibromo-2-phenylcyclopropane and its substituted counterpart toward to 0.5 eqv. amount of $Cr(CO)_6$ in DMSO were executed to determine the possible mechanism. The reaction mixtures were heated at 130 °C for 15 min, quenched with ice-water, extracted with *n*-hexane followed by GC-MS analysis. The ratio of allene areas was used to estimate the relative formation rate. The correlation between the relative rate vs. Hammett constants (σ^+) of the specific substituent on the phenyl ring gives $\rho = -0.55$ with coefficient of 0.949 (Table 2, Fig. 2). The small and negative ρ value implies that the carbon bearing two bromines accepts a nucleophile, $Cr(CO)_6$, in the initial stage which is influenced by the remote substituent.[13] The similar effect on that carbon is also observed from the study of the substituent function of C-13 chemical shifts.[14]

Same conditions were applied on the on the dibromo-[n,1,0]cycloalkanes (n = 3 ~ 6). The progress of reaction between 7,7-dibromobicylo[4.1.0]heptane (**4b**) and $Cr(CO)_6$ was also monitored by using GC/MS analysis (Fig. 3). The identity of monobromocyclopropane **5b** was verified via the comparison the retention time with product obtained from reduction of **4a** using dimethylphosphite in DMSO

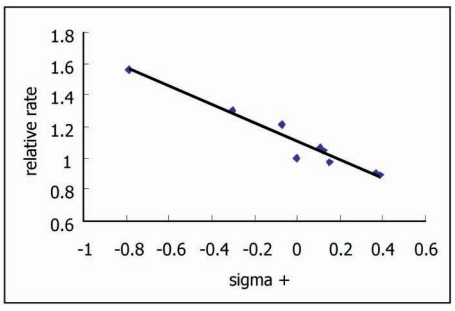

Fig. 2. The correlation between relative rate and the Hammett substituent constant (σ^+) for the formation of arylallenes.

Table 2. Relative rate for the formation of arylallene from the reaction of 1,1-dibromo-2-arylcyclopropanes and $Cr(CO)_6$ in DMSO at 130 °C

Compound (R)	σ^+	Relative rate
4-OCH_3 (**3e**)	-0.79	1.56
4-CH_3 (**3c**)	-0.31	1.30
3-CH_3 (**3b**)	-0.07	1.18
H (**3a**)	0	1.00
4-Cl (**3i**)	0.11	1.07
3-OCH_3 (**3d**)	0.12	1.05
4-Br (**3g**)	0.15	0.97
3-Cl (**3 h**)	0.37	0.90
3-Br (**3f**)	0.39	0.89

solution.[15] The additional isobaric signal can be concluded as 3-bromocycloheptene **6c** by comparing the retention time of the product from allylic bromination of cycloheptene by using *N*-bromosuccinimde (NBS).[16] The reactant complete disappeared within first hours with formation of monoboromocyclopropane **5b** and bromocycloalkene **6b**. The significantly amount of coupling product formed along with vinyl bromide **6b** after 3 h. After work-up, the isolated compounds were subjected to spectral analysis. The molecular weights of resultant obtained from **4b**, **4c** are corresponding to the coupling products and the NMR spectra of **7b** and **7c** are consisting with the literature report.[17] By comparing the pattern of NMR spectrum of **7d** with that of compound **7b** and **7c**, along with its molecular weight (*m/z* 246), we can conclude **7d** is also a coupling product. The product obtained from **4a** is different from other medium ring counterpart. A molecular ion of **7a** appears 320 amu along with the satellites of 318 amu and 322

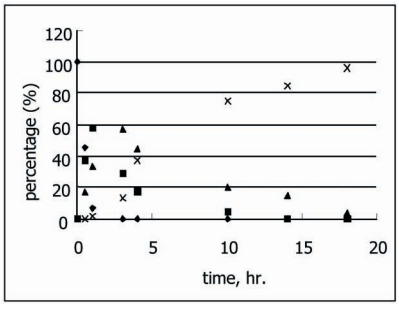

Fig. 3. Concentrations of **5b**, **6b**, and **7b** with time during the reaction of **4b** and $Cr(CO)_6$ at 130 °C. ◆: 7,7-dibromobicyclo[4.1.0]heptane, ■: 7-bromobicyclo[4.1.0]heptane, ▲: 1-bromocyclohept-1-ene, ×: 3-(2-cycloheptenyl)cycloheptene. The amounts (yields) of **4b**, **5b**, **6b**, and **7b** were determined by GC-MS analysis.

amu with intensities ratio of 1:2:1 that indicates the presence of two bromine atoms. The ^{1}H NMR spectrum can be divided into two set spectra which corresponding to a mixture of its *meso*- and *dl*-form with equivalent ratio.[18]

From Figs. 1 and 3, we are able to observe that a bromine atom of dibromocyclopropane can be eliminated by $Cr(CO)_6$ to form a monobromocyclopropane intermediate, which is ruptured at C2-C3 bond leading to allene from arylcyclopropanes **1**. The ring-rupture-coupling products were obtained from bicycloalkanes **4**. $Cr(CO)_6$ undergoes an oxidative-addition into carbon-bromine to initiate this series process.[12]

EXPERIMENTAL

General

Experiments were performed under a dry nitrogen atmosphere. ^{1}H and ^{13}C spectra were recorded at 400, and 100 MHz on Bruker Avance-400, respectively, at ambient temperature. Chemical shifts for samples in $CDCl_3$ solution are reported in δ units relative to TMS. High resolution mass spectra were recorded on a Jeol JMS-HX 110 instrument and low mass spectra were obtained from GC/MS (Thermo Focus GC coupled with Thermo Polaris Q) at an ionization potential of 70 eV. A capillary column (Varian, CP-Sil 5 CB, 25 m × 0.25 mm ID) was used to separate the mixture for mass analysis. All dihalocyclopropanes were prepared by the reaction of haloform and corresponding alkene in *n*-hexane with presence of $KOBu^t$.[14] 7-Bromobicyclo[4.1.0]cycloheptane was prepared by reducing of 7,7-dibromobicyclo[4.1.0]heptane according to literature[15] and 3-bromocycloheptene was obtained by allylic bromination of cycloheptene by NBS.[16] All used solvents were dried and degassed prior to reaction. All reagents were commercially available and used as purchased.

General procedure for the reaction of 1,1-dibromo-2-phenylcyclopropanes (1a) and $Cr(CO)_6$

A mixture of dibromocyclopropane (1.0 mmol) and $Cr(CO)_6$ (1.0 mmol) in various solvent (10 mL) in a 25-mL round-flask on an oil-bath was stirred at 130 °C. Upon the progress of reaction, the color of solution become to green color indicated the consumption of Cr(0) complex. After reaction was completed, the mixture was then poured into an ice-water (20 mL) and extracted with *n*-hexane (20 mL × 3). The organic layer was washed with water, dried ($MgSO_4$) and then separated by a silica gel column using *n*-hexane as eluent to give the desired product.

Products **3a**-**3i** were obtained according to this procedure. The spectral data of those compounds were in good agreement with the literature report.

1,2-Propadienylbenzene (3a)[19]

Colorless oil, yield 86%; ^{1}H NMR: δ 5.28 (d, J = 6.8 Hz, 2H), 6.31 (t, J = 6.8 Hz, 1H), 7.32-7.35 (m, 1H), 7.45-7.49 (m, 4H); ^{13}C NMR δ 78.8, 93.9, 126.7, 126.8, 128.6, 133.9, 209.8; EIMS *m/z* 116 ($M^{+\cdot}$, 61%), 115 (100%).

1-Methyl-3-(1,2-propadienyl)benzene (3b)[19]

Colorless oil, yield 75%; ^{1}H NMR: δ 2.37 (s, 3H), 5.16 (d, J = 6.8 Hz, 2H), 6.17 (t, J = 6.8 Hz, 2H), 7.04 (d, J = 7.6 Hz, 1H), 7.06-7.10 (m, 2H), 7.23 (t, J = 7.6 Hz, 1H); ^{13}C NMR δ 21.3, 78.6, 9.9, 123.8, 127.3, 127.7, 128.5,133.8, 138.2, 209.8; EIMS *m/z* 130 ($M^{+\cdot}$, 82%), 115 (100%).

1-Methyl-4-(1,2-propadienyl)benzene (3c)[19]

Colorless oil, yield 79%; ^{1}H NMR: δ 2.35 (s, 3H), 5.14 (d, J = 6.8 Hz, 2H), 6.16 (t, J = 6.8 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 21.1, 78.6, 93.7, 126.6, 129.3, 130.9, 136.6, 209.6; EIMS *m/z* 130 ($M^{+\cdot}$, 92%), 115 (100%).

1-Methoxy-3-(1,2-propadienyl)benzene (3d)[19]

Colorless oil; yield 72%; ^{1}H NMR δ 3.81 (s, 3H), 5.15 (d, J = 6.8 Hz, 2H), 6.14 (t, J = 6.8 Hz, 1H), 6.76 (dd, J = 7.6, 2.0 Hz, 1H), 6.86 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H); ^{13}C NMR δ 55.2, 78.8, 93.9, 111.8, 112.7, 119.4, 129.5, 135.4, 159.8, 209.8; EIMS *m/z* 146 ($M^{+\cdot}$, 100%), 103 (77%).

1-Methoxy-4-(1,2-propadienyl)benzene (3e)[19]

Colorless oil, yield 95%; ^{1}H NMR δ 3.78 (s, 3H), 5.10 (d, J = 6.8 Hz, 2H), 6.11 (t, J = 6.8 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H); ^{13}C NMR δ 55.21, 78.62, 93.27, 114.08, 126.05, 127.67, 158.66, 209.29; EIMS *m/z*: 146 ($M^{+\cdot}$, 100%), 103 9 (86%).

1-Bromo-3-(1,2-propadienyl)benzene (3f)[19]

Colorless oil, yield 78%; ^{1}H NMR δ 5.19 (d, J = 6.8 Hz, 2H), 6.10 (t, J = 6.8 Hz, 1H), 7.14-7.25 (m, 2H), 7.32 (d, J = 7.6 Hz, 1H), 7.45 (s, 1H); ^{13}C NMR δ 79.4, 92.9, 122.7, 125.2, 129.4, 129.7, 130.0, 136.2, 209.9; EIMS *m/z* 196 ($M^{+\cdot}$, 28%), 115 (100%).

1-Bromo-4-(1,2-propadienyl)benzene (3g)[19]

Colorless oil, yield 84%; ^{1}H NMR δ 5.15 (d, J = 6.8 Hz, 2H), 6.11 (t, J = 6.8 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 79.2, 93.2, 120.5, 128.2, 131.7, 132.9, 209.8; EIMS *m/z* 196 ($M^{+\cdot}$, 32%), 115 (100%).

1-Chloro-3-(1,2-propadienyl)benzene (3h)[20]

Colorless oil, yield 83%; ^{1}H NMR δ 5.18 (d, J = 6.8

Hz, 2H), 6.11 (t, *J* = 6.8 Hz, 1H), 7.15-7.25 (m, 3H), 7.29 (s, 1H); ^{13}C NMR δ 79.3, 93.1, 124.8, 126.5, 126.8, 128.7, 134.5, 135.9, 209.9; EIMS *m/z* 152 ($M^{+\cdot}$, 11%), 115 (100%).

1-Chloro-4-(1,2-propadienyl)benzene (3i)[20]

Colorless oil, yield 89%; ^{1}H NMR δ 5.16 (d, *J* = 6.8 Hz, 2H), 6.13 (t, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 79.2, 99.1, 127.8, 128.7, 132.4, 132.5, 209.8; EIMS *m/z* 152 ($M^{+\cdot}$, 12%), 115 (100%).

Attempt to trap the carbene by adding cyclohexene into mixture of dibromocyclopropane (1a) and $Cr(CO)_6$

The experiment was carried out as previous process except for adding cyclohexene (2.0 mmole). After work-up, allene **3a** was observed as only product presence in resultant from the analysis used GC/MS technique.

Competition reaction between $Cr(CO)_6$ toward to 1,1-dibromo-2-phenylcyclopropane and substituted 1,1-dibromo-2-phenylcyclopropane in DMSO solution

The mixture of 1,1-dibromo-2-phenylcyclopropane (127 mg, 0.50 mmol), substituted 1,1-dibromo-2-phenyl-cyclopropane (0.50 mmol) and $Cr(CO)_6$ (1.00 mmol) in DMSO (10.0 mL) with a stir bar in a 25-mL round-bottom flask was put on a pre-heated (130 °C) oil-bath. After 15 min, the resultant was poured into an ice-water (20 mL). The mixture was extracted with *n*-hexane, followed by dried over $MgSO_4$ and subjected to be analyzed by GC/MS. The ratio of area of two allenes was used to estimate their relative rate of formation.

General procedure for the reaction of 1,1-dibromo-bicyclo[n.1.0]alkane 4 and $Cr(CO)_6$ in DMF solution

A mixture of dibromocyclopropane **4** (1.0 mmol) and $Cr(CO)_6$ (1.0 mmol) in DMF (10 mL) in a 25-mL round-flask on an oil-bath was stirred at 130 °C for 18 h. Upon the progress of reaction, the color of solution become to green color indicated the consumption of Cr(0) complex. After the reaction was completed, the mixture was then poured into an ice-water (20 mL) and extracted with *n*-hexane (20 mL × 3). The organic layer was washed with water, dried ($MgSO_4$) and then separated by pass through a silica gel column using *n*-hexane as eluent to give the desired product. The spectral data of **7a**-**7c** were in good agreement with the literature report.

2-Bromo-3-(2′-bromo-2′-cyclohexeyl)cyclohexene (7a)[18]

Colorless oil, yield 87%; ^{1}H NMR δ 1.42-1.65 (m, 8H), 1.65-1.95 (m, 8H), 1.95-2.15 (m, 8H), 2.82-2.95 (m, 2H), 3.15-3.25 (m, 2H), 6.11-6.18 (m, 2H), 6.20-6.28 (m, 2H); ^{13}C NMR δ 21.4, 21.5, 24.4, 27.7, 27.9, 28.8, 44.2, 45.7, 127.0, 127.3, 131.9, 132.7; EIMS *m/z* 322/320 ($M^{+\cdot}$, 3%/3%), 79 (100%).

3-(2-Cycloheptenyl)cycloheptene (7b)[17]

Colorless oil, yield 84%; ^{1}H NMR δ 1.00-2.40 (m, 18H, 5.50-5.70 (m, 2H), 5.70-5.90 (m, 2H); ^{13}C NMR δ 26.9, 28.7, 30.5, 31.0, 31.3, 31.4, 45.4, 45.9, 131.5, 131.8, 136.3, 136.6; EIMS *m/z* 190 ($M^{+\cdot}$, 0.3%), 95 (100%).

3-(2-Cycloocteyl)cyclooctene (7c)[17]

Colorless oil, yield 75%; ^{1}H NMR δ 0.80-2.50 (m, 22H), 5.20-5.40 (m, 2H), 5.60-5.75 (m, 2H); ^{13}C NMR δ 25.8, 25.9, 26.8, 26.8, 27.1, 27.1, 28.6, 29.5, 29.7, 34.3, 40.7, 40.9, 129.2, 129.4,133.3, 134.4; EIMS *m/z* 218 ($M^{+\cdot}$, 3%), 67 (100%).

3-(2-Cyclononeyl)cyclononene (7d)

Colorless oil, yield 80%; ^{1}H NMR δ 1.00-2.50 (m, 26H), 5.10-5.30 (m, 2H), 5.40-5.65 (m, 2H); ^{13}C NMR δ 24.8, 24.9, 25.6, 25.8, 26.0, 26.1, 26.1, 26.4, 26.5, 42.0, 42.5, 128.8, 129.2, 134.0, 134.9; EIMS *m/z* 246 ($M^{+\cdot}$, 2%), 81 (100%); HRMS calcd for $C_{18}H_{30}$ 246.2348, found 246.1262.

ACKNOWLEDGEMENTS

Financial support by the National Science of the Republic of China (NSC 94-2113-M-126-005) and the technique supporting by NCHC are gratefully acknowledged.

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