



## Reaction of Aromatic and Unsaturated Compounds with the Potassium Permanganate/HCl (HBr) Acetonitrile Reagent

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Addition of hydrochloric or hydrobromic acid to a solution of potassium permanganate in acetonitrile produced a homogeneous mixture, which is suitable for laboratory chlorination or bromination, respectively. Aromatic compounds more reactive than alkylbenzenes can be chlorinated or brominated without additional catalyst. Alkenes and alkynes give the corresponding *vicinal* dihaloalkanes and vinyl halides. All reactions complete within two hours under mild condition (25-60 °C) with excellent to moderate yields.

### INTRODUCTION

During the studies of potassium permanganate/triethylamine oxidation,<sup>1,2</sup> we encountered the halogenation of electrophilic substances. With some improvement a reagent suitable for chlorination in the laboratory was developed. The classical direct halogenation<sup>3</sup> (chlorination or bromination) of aromatic systems is wasteful in being that one half of the halogen ends up as hydrogen halide. The use of gaseous chlorine and liquid bromine in large-scale operations causes environmental hazard as well as economic problem such as corrosion of equipments. Several oxidative processes<sup>4-7</sup> have been recently described for the halogenation of organic compounds. In these reactions a hydrogen halide is oxidized by the oxidant *in situ* with the subsequent formation of organic halides. Oxidative halogenation of the type such as  $\text{H}_2\text{O}_2/\text{HBr}$  (HCl) have been used for the preparation of *vicinal* dihalides from alkenes<sup>6,7</sup> and for the bromination of the aromatic compounds.<sup>6</sup> But they required the presence of phase transfer catalyst (TBAB) and a cosolvent system.<sup>6,7</sup> Moreover, large excess of HCl (6x) was needed; and chlorohydrin formation<sup>7</sup> reduced the yield of *vicinal* dichlorides considerably. Potassium permanganate has been widely studied,<sup>8</sup> and is an important oxidative reagent in organic synthesis.<sup>9</sup> Manganese(VII) has been used in combination with iodide and iodine in electrophilic iodinations.<sup>5,10</sup> When aromatic compounds, olefins and alkynes are the substrates of halogenations, the problem of these reactions concerns stabilization of the manganese halide complex in a homogeneous stage. The problem can be solved by using acetonitrile as solvent owing to its compatible attributes such as solvation power. In the present work we report the chlorination of electrophilic substrates with  $\text{KMnO}_4/\text{HCl}/\text{CH}_3\text{CN}$  reagent, which reveals excellent stability and homogeneity. Furthermore, its usefulness in aromatic chlorination and preparations of dihaloalkanes and *vicinal* dichloroalkenes

from alkenes and alkynes via addition is demonstrated. On replacing of hydrochloric acid with hydrobromic acid, the corresponding brominated compounds can also be prepared from the homogeneous  $\text{KMnO}_4/\text{HBr}/\text{CH}_3\text{CN}$  reagent.

### RESULTS AND DISCUSSION

When hydrochloric acid is added to potassium permanganate in acetonitrile, a homogeneous, green solution results. This solution is effective for electrophilic aromatic chlorination. Chlorination occurs readily with substrates which are activated toward electrophilic substitution at room temperature. Mildly activated compounds such as alkylbenzenes were recovered unchanged, but they underwent chlorination smoothly at 60 °C. Aromatics with electron-withdrawing groups are unreactive.

Chlorination of aniline and phenol with the  $\text{KMnO}_4/\text{HCl}$  acetonitrile reagent gave mixtures of dichlorinated products. The yield from aniline was moderate (48%), consisting of 19% 2,4- and 29% of the 2,6-dichloroanilines. A higher yield (88%) was obtained from phenol, the product being an equimolar mixture of 2,4- and 2,6-dichlorophenols. Toluene was converted to chlorotoluene at 60 °C in 81% yield with an *ortho/para* ratio of 2:3. Chloroethylbenzene was obtained in 85% yield with an *ortho/para* ratio of 1:2. Anisole gave an *ortho/para* distribution of 3/2 in 91% total yield. In general, the *ortho/para* ratio obtained was almost the same as the non-catalytic chlorination carrying out in acetonitrile.<sup>11</sup> Anisole and phenol gave higher *ortho/para* ratio presumably due to at least part of the reaction proceeding from complexes formed between manganese and the oxygen atom. Anthracene was readily chlorinated by  $\text{KMnO}_4/\text{HCl}$  to 9,10-dichloroanthracene together with 5% anthraquinone. Naphthalene yielded only 1-chloronaphthalene, which is the normal product of Lewis acid

catalyzed chlorination of this condensed ring system. No isomerization to the 2-isomer was apparent. Table 1 presents a summary of results. Although moderate to excellent yields (48-95%) are obtained, it is a convenient laboratory procedure which can be accomplished within 2 hours.

A similar condition is applicable for achieving bromination. Typical yields are summarized in Table 2. Bromination of aniline, *N,N*-dimethylaniline and phenol with the  $\text{KMnO}_4/\text{HBr}/\text{CH}_3\text{CN}$  reagent gave only 2,4,6-tribrominated products due to the presence of activating substituents and the higher reactivity of this brominating system. Toluene was converted to bromotoluenes in 84% yield with an *ortho/para* ratio of 2:1. An 80% yield of bromoanisole was obtained with an *ortho/para* ratio of 4/1. While conventional bromination favors *para*-substitution,<sup>3</sup> our observation of an *ortho* selectivity probably is due to complexation between manganese and the methoxy oxygen which renders the *ortho* substitution preferable to the less sterically hindered *para* position. Complexation involving manganese in higher oxidation stage is indicated by the fact that the combination of hydrobromic acid and  $\text{MnBr}_2$  in acetonitrile is not an effective brominating agent. Naphthalene and anthracene were converted to 1-bromonaphthalene and 9,10-dibromoanthracene by reaction with  $\text{KMnO}_4/\text{HBr}/\text{CH}_3\text{CN}$  reagent, respectively.

Olefinic compounds including styrenes, allylbenzene and cinnamyl alcohol reacted with the  $\text{KMnO}_4/\text{HX}/\text{CH}_3\text{CN}$  reagent, the sole products being the corresponding vicinal dihalo compounds. Such results stand in sharp contrast to halogenation of aromatic compound in which mixture of products were obtained. These results are attributed to the more rapid addition to the side chain double bond than halogenation of the aromatic ring. However, with 1-allyl-3,4-methylenedioxybenzene and 1,2-methylenedioxy-4-propenylbenzene the halogenation of the aromatic ring oc-

Table 1. Aromatic Chlorides Obtained by Using  $\text{KMnO}_4/\text{HCl}/\text{CH}_3\text{CN}$  Reagent

Entry	Substrates	Products	Isolated yields (%)
1	aniline	2,4-dichloroaniline	19
		2,6-dichloroaniline	29
2	phenol	2,4-dichlorophenol	44
		2,6-dichlorophenol	44
3	toluene	2-chlorotoluene	32
		4-chlorotoluene	49
4	ethylbenzene	2-chloroethylbenzene	28
		4-chloroethylbenzene	57
5	anisole	2-chloroanisole	55
		4-chloroanisole	36
6	naphthalene	1-chloronaphthalene	82
7	anthracene	9,10-dichloroanthracene	90
		anthraquinone	5

curred, due to the presence of strong electron donating substituents (Tables 3 and 4). It is noteworthy that no oxidation of the alcohol function has been observed with cinnamyl alcohol.  $\alpha,\beta$ -Unsaturated ketone such as mesityl oxide was also halogenated by this reagent to the corresponding 1,2-dichloro or dibromo compounds without affecting the ketone function.

Using conditions similar to those used for aromatic compounds, the  $\text{KMnO}_4/\text{HCl}/\text{CH}_3\text{CN}$  reagent is applicable for the preparation of vinyl dichlorides from alkynes; frequently with yields better than the conventional chlorination of alkynes.<sup>12,13</sup> Products were easily purified by column chromatography to eliminate the unreacted starting alkynes. The regiochemistry has been determined based on the  $^{13}\text{C}$  chemical shift<sup>14,15</sup> of the vinylic carbon that bears the chlorine atom (Table 5). By comparison with literature values<sup>12,13,16</sup> the stereochemistry of each product was determined. The major product found in each isomeric 1,2-di-

Table 2. Aromatic Bromides Obtained by Using  $\text{KMnO}_4/\text{HBr}/\text{CH}_3\text{CN}$  Reagent

Entry	Substrates	Products	Isolated yields (%)
1	<i>N,N</i> -dimethylaniline	2,4,6-tribromo- <i>N,N</i> -dimethylaniline	95
2	aniline	2,4,6-tribromoaniline	92
3	phenol	2,4,6-tribromophenol	97
4	toluene	2-bromotoluene	56
		4-bromotoluene	28
5	anisole	2-bromoanisole	64
		4-bromoanisole	16
6	naphthalene	1-bromonaphthalene	71
7	anthracene	9,10-dibromoanthracene	85
		anthraquinone	3

Table 3. Dichloroalkanes Obtained by Using KMnO<sub>4</sub>/HCl/CH<sub>3</sub>CN Reagent

Entry	Substrates	Products	Isolated yields (%)
1	styrene	1,2-dichloro-1-phenylethane	88
2	$\alpha$ -methylstyrene	1,2-dichloro-1-phenylpropane	79
3	1-allyl-3,4-methylene-dioxybenzene	2-(1,2-dichloropropyl)-4,5-methylenedioxy-1-chlorobenzene	85
4	1,2-methylenedioxy-4-propenylbenzene	2-(2,3-dichloropropyl)-4,5-methylenedioxy-1-chlorobenzene	83
5	cyclohexene	1,2-dichlorocyclohexane	74
6	4-vinyl-1-cyclohexene	4-(1,2-dichloroethyl)-1,2-dichloro-cyclohexane	71
7	mesityl oxide	2-methyl-2,3-dichloropropyl methyl ketone	55
8	tetramethylethylene	2,3-dichloro-2,3-dimethylbutane	73
9	allylbenzene	2,3-dichloropropylbenzene	69
10	cinnamyl alcohol	2,3-dichloro-3-phenyl-1-propanol	73

chloroalkenes is the (*E*)- $\alpha,\beta$ -dichloro alkene (Table 5) arising from anti addition to the triple bond. Unlike the conventional chlorination, where anti addition predominant, both syn and anti modes of addition are observed in this case. Phenyl substitution usually increase the *E/Z* ratio of the product.

Reaction of alkynes with the KMnO<sub>4</sub>/HBr/CH<sub>3</sub>CN reagent at 60 °C gave only the corresponding (*E*)-dibromoalkenes in excellent yields. Typical results are shown in Table 6. Stereochemistry were determined by calculation of the <sup>1</sup>H and <sup>13</sup>C chemical shifts of the vinylic carbon that bears the bromine atom; and by comparison with literature values.<sup>12,13,16</sup> Therefore, KMnO<sub>4</sub>/HBr in acetonitrile is the cleanest, the most convenient, and the most direct system re-

ported to date for preparation of vinyl dibromides.

## CONCLUSION

In conclusion we have developed a convenient laboratory chlorination procedure from the easily available, non-toxic and economic hydrochloric acid-potassium permanganate-acetonitrile. This reagent is not only suitable for aromatic chlorination without additional catalyst, but is also applicable for preparation of vicinal dichloroalkanes and dichloroalkenes from a variety of alkenes and alkynes. Bromination can be carried out by replacing hydrochloric acid with hydrobromic acid. Moreover, bromination of al-

Table 4. Dibromoalkanes Obtained by Using KMnO<sub>4</sub>/HBr/CH<sub>3</sub>CN Reagent

Entry	Substrates	Products	Isolated yields (%)
1	styrene	1,2-dibromo-1-phenylethane	90
2	$\alpha$ -methylstyrene	1,2-dibromo-1-phenylpropane	81
3	1-allyl-3,4-methylene-dioxybenzene	2-(1,2-dibromopropyl)-4,5-methylenedioxy-1-bromobenzene	91
4	1,2-methylenedioxy-4-propenylbenzene	2-(2,3-dibromopropyl)-4,5-methylenedioxy-1-bromobenzene	88
5	cyclohexene	1,2-dibromocyclohexane	83
6	4-vinyl-1-cyclohexene	4-(1,2-dibromoethyl)-1,2-dibromocyclohexane	87
7	mesityl oxide	2-methyl-2,3-dibromopropyl methyl ketone	61
8	tetramethylethylene	2,3-dibromo-2,3-dimethylbutane	80
9	allylbenzene	2,3-dibromopropylbenzene	88
10	cinnamyl alcohol	2,3-dibromo-3-phenyl-1-propanol	88

Table 5. Dichloroalkenes Obtained by Using  $\text{KMnO}_4/\text{HCl}/\text{CH}_3\text{CN}$  Reagent

Entry	Substrates	Products	<i>Z/E</i> <sup>a</sup>	Isolated yields (%)
1	1-nonyne	1,2-dichloro-1-nonene	2/5	76
2	1-dodecyne	1,2-dichloro-1-dodecene	2/3	70
3	2-methyl-3-butyne-2-ol	3,4-dichloro-2-methyl-3-buten-2-ol	2/5	63
4	phenylacetylene	$\alpha,\beta$ -dichlorostyrene	1/3	74
5	1-phenyl-1-propyne	$\alpha,\beta$ -dichloro- $\alpha$ -methylstyrene	1/4	77
6	4-octyne	4,5-dichloro-4-octene	1/3	75
7	diphenylacetylene	1,2-dichloro-1,2-diphenylethylene	1/5	73

<sup>a</sup> Ratio was determined by analysis of the  $^1\text{H}$  NMR spectrum of crude products.Table 6. Dibromoalkenes Obtained by Using  $\text{KMnO}_4/\text{HBr}/\text{CH}_3\text{CN}$  Reagent

Entry	Substrates	Products	Isolated yields (%)
1	1-nonyne	( <i>E</i> )-1,2-dibromo-1-nonene	85
2	1-dodecyne	( <i>E</i> )-1,2-dibromo-1-dodecene	93
3	phenylacetylene	( <i>E</i> )- $\alpha,\beta$ -dibromostyrene	93
4	1-phenyl-1-propyne	( <i>E</i> )- $\alpha,\beta$ -dibromo- $\alpha$ -methylstyrene	87
5	4-octyne	( <i>E</i> )-4,5-dibromo-4-octene	86
6	diphenylacetylene	( <i>E</i> )-1,2-dibromo-1,2-diphenylethylene	90

kynes give vinylic dibromides solely in the (*E*)-configuration. As to the operation procedure, bromination is just as convenient as the chlorination procedure.

## EXPERIMENTAL SECTION

IR spectra (neat or KBr pellet) were run on a JASCO-IR-700 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded on JEOL-JNM-EX 400 spectrometer; chemical shifts are reported in parts per million downfield from TMS. Mass spectra (EI) were recorded on either a JEOL-JMS-D-300 or a Finnigan TSQ-700 mass spectrometer, operating at an ionizing voltage of 70 eV. Melting points were recorded on a Mel-temp. instrument and were uncorrected.

$\text{KMnO}_4$ , HBr and HCl (E. Merck, analytical grade) were used without purification. Aromatic compounds, alkenes and alkynes (Aldrich, reagent grade) were purified by distillation or recrystallization before use.

### General Procedure for the Preparation of Aromatic Chlorides

$\text{KMnO}_4$  (0.474 g, 3 mmol) and  $\text{CH}_3\text{CN}$  (100 mL) were mixed in a round-bottomed flask under magnetic stirring, followed by addition of HCl (37%, 3.8 mL, 45 mmol) and stirred for 5 min. After addition of the substrate (10 mmol)

stirring was continued until the solution turned colorless. Alkylbenzenes, anisole and naphthalene were chlorinated at 60 °C. The progress of reaction was monitored by TLC (silica gel,  $\text{CHCl}_3$  as eluent). After the solvent was removed under vacuum,  $\text{CHCl}_3$  (40 mL) was added to the mixture, and the colloidal salts was filtered. After evaporation of the filtrate, separation of products was achieved by passing through a column of silica gel (2.5 cm  $\times$  25 cm, E. Merck 70-230 mesh) using  $\text{CHCl}_3$ /hexane (1:1) as eluents to give the pure products. Products from toluene, ethylbenzene and anisole were purified by distillation.

### General Procedure for the Preparation of Aromatic Bromides

The bromination of the corresponding aromatic compounds (10 mmol) was carried out similarly to that described for the preparation of aromatic chlorides, except that  $\text{KMnO}_4$  (0.632 g, 4 mmol) in  $\text{CH}_3\text{CN}$  (100 mL) and HBr (47%, 6.8 mL, 60 mmol) were used.

### General Procedure for the Preparation of Dichloroalkenes

The addition of chlorine to alkenes (10 mmol) or 1-allyl-3,4-methylenedioxybenzene (0.97 g, 6 mmol) or 1,2-methylenedioxy-4-propenylbenzene (0.97 g, 6 mmol) or 4-vinyl-1-cyclohexene (0.65 mL, 5 mmol) was carried out

similarly as described under the preparation of aromatic chlorides.

### 1-Chloro-2-(1,2-dichloropropyl)-4,5-methylenedioxybenzene

IR  $\nu_{\max}$  (neat) 2902, 1480, 1239, 1039, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.00 (s, 1H, aromatic H *ortho* to Cl), 6.81 (s, 1H, aromatic H *meta* to Cl), 5.98 (s, 2H,  $\text{OCH}_2\text{O}$ ), 4.46 (m, 1H,  $\text{CHCl}$ ), 3.86 (dd, 1H,  $\text{CHH}'\text{Cl}$ ,  $J = 4.4, 10.0$  Hz), 3.72 (dd, 1H,  $\text{CHH}'\text{Cl}$ ,  $J = 10.0, 2.9$  Hz), 3.62 (dd, 1H,  $\text{ArCHH}'$ ,  $J = 14.6, 4.9$  Hz), 3.01 (dd, 1H,  $\text{ArCHH}'$ ,  $J = 14.6, 9.3$  Hz); MS  $m/z$  (rel intensity) 266 ( $\text{M}^+$ , 30), 268 ( $\text{M}+2$ , 30), 270 ( $\text{M}+4$ , 10); Anal. Calcd. for  $\text{C}_{10}\text{H}_9\text{Cl}_3\text{O}_2$ : C, 44.89; H, 3.39; Found: C, 44.79; H, 3.41.

### 1-Chloro-2-(2,3-dichloropropyl)-4,5-methylenedioxybenzene

IR  $\nu_{\max}$  (neat) 2902, 1480, 1235, 1040  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.04 (s, 1H, aromatic H *ortho* to Cl), 6.83 (s, 1H, aromatic H *meta* to Cl), 6.01 (s, 2H,  $\text{OCH}_2\text{O}$ ), 5.45 (d, 1H,  $\text{ArCHCl}$ ,  $J = 7.8$  Hz), 4.36 (m, 1H,  $\text{CHClCH}_3$ ), 1.69 (d, 3H,  $\text{CH}_3$ ,  $J = 6.3$  Hz); MS  $m/z$  (rel intensity) 266 ( $\text{M}^+$ , 70), 268 ( $\text{M}+2$ , 70), 270 ( $\text{M}+4$ , 23); Anal. Calcd. for  $\text{C}_{10}\text{H}_9\text{Cl}_3\text{O}_2$ : C, 44.89; H, 3.39; Found: C, 44.82; H, 3.38.

### 2,3-Dichloro-3-phenyl-1-propanol

IR  $\nu_{\max}$  (neat) 3412, 2960, 1490, 1247, 1034, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.4 (m, 5H, aromatic H), 5.09 (d, 1H,  $\text{ArCHCl}$ ,  $J = 11.2$  Hz), 4.40 (m, 1H,  $\text{CHCl}$ ), 4.22 (m, 2H,  $\text{CH}_2\text{OH}$ ), 2.60 (br, 1H, OH); MS  $m/z$  (rel intensity) 204 ( $\text{M}^+$ , 25), 206 ( $\text{M}+2$ , 16), 208 ( $\text{M}+4$ , 8); Anal. Calcd. for  $\text{C}_9\text{H}_{10}\text{Cl}_2\text{O}$ : C, 52.71; H, 4.91; Found: C, 52.83; H, 4.88.

### General Procedure for the Preparation of Dibromoalkanes

The addition of bromine to alkenes (10 mmol) or 1-allyl-3,4-methylenedioxybenzene (0.97 g, 6 mmol) or 1,2-methylenedioxy-4-propenylbenzene (0.97 g, 6 mmol) or 4-vinyl-1-cyclohexene (0.65 mL, 5 mmol) was carried out similarly as that described under the preparation of aromatic chlorides, except that  $\text{KMnO}_4$  (0.395 g, 2.5 mmol) in  $\text{CH}_3\text{CN}$  (100 mL) and HBr (47%, 4.2 mL, 37 mmol) were used.

### 1-Bromo-2-(1,2-dibromopropyl)-4,5-methylenedioxybenzene

IR  $\nu_{\max}$  (neat) 2829, 1477, 1235, 1039, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.89 (s, 1H, aromatic H *ortho* to Br), 6.70 (s, 1H, aromatic H *meta* to Br), 5.87 (s, 2H,  $\text{OCH}_2\text{O}$ ), 4.35 (m, 1H,  $\text{CHBr}$ ), 3.75 (dd, 1H,  $\text{CHH}'\text{Br}$ ,  $J = 4.4, 10.7$  Hz),

3.60 (dd, 1H,  $\text{CHH}'\text{Br}$ ,  $J = 10.7, 3.0$  Hz), 3.50 (dd, 1H,  $\text{ArCHH}'$ ,  $J = 14.5, 4.8$  Hz), 2.89 (dd, 1H,  $\text{ArCHH}'$ ,  $J = 14.5, 9.2$  Hz); MS  $m/z$  (rel intensity) 398 ( $\text{M}^+$ , 8), 400 ( $\text{M}+2$ , 25), 402 ( $\text{M}+4$ , 25), 404 ( $\text{M}+6$ , 8); Anal. Calcd. for  $\text{C}_{10}\text{H}_9\text{Br}_3\text{O}_2$ : C, 30.16; H, 2.28; Found: C, 30.21; H, 2.33.

### General Procedure for the Preparation of Vinyl Dichlorides

The addition of chlorine to alkynes (10 mmol) was carried out similarly as that described under the preparation of aromatic chloride, except that  $\text{KMnO}_4$  (0.395 g, 2.5 mmol) in  $\text{CH}_3\text{CN}$  (100 mL) and HCl (37%, 3.1 mL, 37 mmol) were used. An additional stirring of 45 to 120 min at 60 °C was needed after addition of the substrate completed. When a mixture of (*E*)- and (*Z*)-products was obtained, separation into the components could be achieved by chromatography through a column of silica gel (2.5 cm  $\times$  20 cm, E. Merck 230-400 mesh) using  $\text{CHCl}_3$ /hexane (1/3) as eluents.

### (*E*)-1,2-Dichloro-1-nonene

IR  $\nu_{\max}$  (neat) 3070, 2930, 1465, 753  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.73 (s, 1H,  $=\text{C}-\text{H}$ ), 2.72 (t, 2H,  $=\text{C}-\text{CH}_2$ ,  $J = 7.3$  Hz), 1.50 (m, 2H,  $=\text{C}-\text{CH}_2-\text{CH}_2$ ), 1.30 (m, 8H,  $4\text{CH}_2$ ), 0.80 (t, 3H,  $\text{CH}_3$ ,  $J = 6.8$  Hz); MS  $m/z$  (rel intensity) 194 ( $\text{M}^+$ , 30), 196 ( $\text{M}+2$ , 20), 198 ( $\text{M}+4$ , 3); Anal. Calcd. for  $\text{C}_9\text{H}_{16}\text{Cl}_2$ : C, 55.65; H, 8.31; Found: C, 55.57; H, 8.40.

### (*Z*)-1,2-Dichloro-1-nonene

IR  $\nu_{\max}$  (neat) 3071, 2930, 1465, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.12 (s, 1H,  $=\text{C}-\text{H}$ ), 2.50 (t, 2H,  $=\text{C}-\text{CH}_2$ ,  $J = 7.3$  Hz), 1.55 (m, 2H,  $=\text{C}-\text{CH}_2-\text{CH}_2$ ), 1.30 (m, 8H,  $4\text{CH}_2$ ), 0.80 (t, 3H,  $\text{CH}_3$ ,  $J = 6.3$  Hz); MS  $m/z$  (rel intensity) 194 ( $\text{M}^+$ , 20), 196 ( $\text{M}+2$ , 14), 198 ( $\text{M}+4$ , 2); Anal. Calcd. for  $\text{C}_9\text{H}_{16}\text{Cl}_2$ : C, 55.65; H, 8.31; Found: C, 55.70; H, 8.33.

### (*E*)-1,2-Dichloro-1-dodecene

IR  $\nu_{\max}$  (neat) 3020, 2928, 1465, 754  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.80 (s, 1H,  $=\text{C}-\text{H}$ ), 2.80 (t, 2H,  $=\text{C}-\text{CH}_2$ ,  $J = 7.3$  Hz), 1.45 (m, 2H,  $=\text{C}-\text{CH}_2-\text{CH}_2$ ), 1.33 (m, 14H,  $7\text{CH}_2$ ), 0.88 (t, 3H,  $\text{CH}_3$ ,  $J = 6.8$  Hz); MS  $m/z$  (rel intensity) 236 ( $\text{M}^+$ , 15), 238 ( $\text{M}+2$ , 10), 240 ( $\text{M}+4$ , 2); Anal. Calcd. for  $\text{C}_{12}\text{H}_{22}\text{Cl}_2$ : C, 60.99; H, 9.39; Found: C, 60.88; H, 9.42.

### (*Z*)-1,2-Dichloro-1-dodecene

IR  $\nu_{\max}$  (neat) 3020, 2928, 1464, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.13 (s, 1H,  $=\text{C}-\text{H}$ ), 2.48 (t, 2H,  $=\text{C}-\text{CH}_2$ ,  $J = 7.3$  Hz), 1.40 (m, 2H,  $=\text{C}-\text{CH}_2-\text{CH}_2$ ), 1.30 (m, 14H,  $7\text{CH}_2$ ), 0.88 (t, 3H,  $\text{CH}_3$ ,  $J = 6.8$  Hz); MS  $m/z$  (rel intensity) 236 ( $\text{M}^+$ , 12), 238 ( $\text{M}+2$ , 8), 240 ( $\text{M}+4$ , 1); Anal. Calcd. for  $\text{C}_{12}\text{H}_{22}\text{Cl}_2$ : C, 60.99; H, 9.39; Found: C, 60.98; H, 9.45.

### General Procedure for the Preparation of Vinyl Dibromides

The addition of bromine to alkynes (10 mmol) was carried out similarly as that describes under the preparation of aromatic chloride, except that  $\text{KMnO}_4$  (0.474 g, 3 mmol) in  $\text{CH}_3\text{CN}$  (100 mL) and  $\text{HBr}$  (47%, 5.1 mL, 45 mmol) were used. After an additional stirring for 30 to 120 min at 60 °C, the solution turned colorless; and the usual purification procedures were carried to obtain the pure product.

#### (E)-1,2-Dibromo-1-nonene

IR  $\nu_{\text{max}}$  (neat) 3090, 2928, 1461, 753, 689  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  6.40 (s, 1H, =C-H), 2.59 (t, 2H, =C-CH<sub>2</sub>,  $J$  = 7.3 Hz), 1.50 (m, 2H, =C-CH<sub>2</sub>-CH<sub>2</sub>), 1.35 (m, 8H, 4CH<sub>2</sub>), 0.89 (t, 3H, CH<sub>3</sub>,  $J$  = 6.9 Hz); MS  $m/z$  (rel intensity) 282 ( $\text{M}^+$ , 39), 284 ( $\text{M}+2$ , 80), 286 ( $\text{M}+4$ , 40); Anal. Calcd. for  $\text{C}_9\text{H}_{16}\text{Br}_2$ : C, 38.30; H, 5.72; Found: C, 38.25; H, 5.81.

#### (E)-1,2-Dibromo-1-dodecene

IR  $\nu_{\text{max}}$  (neat) 3092, 2928, 1462, 754  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$  6.32 (s, 1H, =C-H), 2.51 (t, 2H, =C-CH<sub>2</sub>,  $J$  = 7.3 Hz), 1.45 (m, 2H, =C-CH<sub>2</sub>-CH<sub>2</sub>), 1.23 (m, 14H, 7CH<sub>2</sub>), 0.81 (t, 3H, CH<sub>3</sub>,  $J$  = 6.3 Hz); MS  $m/z$  (rel intensity) 324 ( $\text{M}^+$ , 10), 326 ( $\text{M}+2$ , 20), 328 ( $\text{M}+4$ , 10); Anal. Calcd. for  $\text{C}_{12}\text{H}_{22}\text{Br}_2$ : C, 44.44; H, 6.84; Found: C, 44.40; H, 6.84.

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### Key Words

Aryl halides; Vicinal dihaloalkanes; Vinyl dihalides; Potassium permanganate; Hydrochloric

acid; Hydrobromic acid.

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