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Transformation of Ketones and Aldehydes to *gem*-Dihalides via Hydrazones Using Copper(II) Halides

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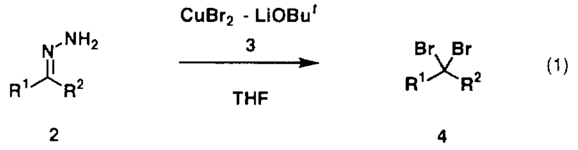
Abstract: Preparation of *gem*-dihalides by the oxidation of hydrazones, which were easily prepared by the treatment of ketones and aldehydes with hydrazine hydrate in the presence of molecular sieves 4A, with copper(II) compounds was studied. The treatment of hydrazones with copper(II) bromide-lithium *tert*-butoxide in THF gave the corresponding *gem*-dibromides in good yields. *gem*-Dichlorides were also obtained by the similar reaction of hydrazones using copper(II) chloride-lithium *tert*-butoxide as an oxidizing agent. Furthermore it was found that the same transformations were conveniently achieved by the use of copper(II) halides-triethylamine in methanol. Copyright © 1996 Elsevier Science Ltd

Organic halides play important roles in organic synthesis as intermediates for construction of various carbon-based structures. Of a variety of such compounds, *gem*-dihalides are used in the preparation of acetylenic compounds,[1] α-halo organometallics,[2] and reagents for carbonyl olefination.[3] The synthetic application of these dihalides, however, are largely restricted because their selective preparation is generally difficult owing to the formation of vinyl halides as by-products. The widely used procedures for the preparation of these halides are those using carbonyl compounds as starting materials. The preparation of *gem*-difluorides, which are relatively stable congeners, can be achieved without difficulty by the treatment of carbonyl compounds with hydrogen fluoride-diethylaminosulfur trifluoride[4] or selenium tetrafluoride.[5] Although the synthesis of *gem*-dichloride using phosphorous pentachloride[6] or thionyl chloride[7] have been developed, the formation of vinyl chlorides becomes a serious side reaction especially when the reaction is performed at an elevated temperature. The formation of *gem*-dibromides was observed in the reaction of aromatic aldehydes with boron tribromide,[8] and the transformation of a certain ketone to the *gem*-dibromide by the treatment with phosphorous pentabromide[9] was reported. These methods, however, seem to be applicable only to the preparation of *gem*-dibromide which has no β-hydrogen or whose structure is such that the corresponding vinyl bromide is excessively strained. Although the oxidative halogenations of hydrazones with halogens were studied,[10] the dihalides other than fluorides[10a] were obtained in poor yields.

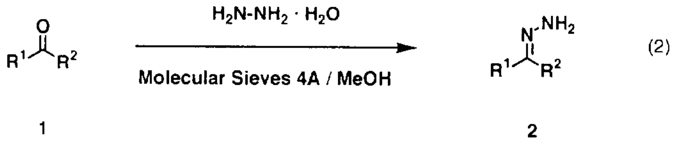
The synthesis of *gem*-dihalides is also achieved by the addition of hydrogen halides to alkynes, allenes, and vinyl halides,[11] and the reactions of 1,1-dihaloalkyllithiums with alkyl halides and carbonyl compounds.[2] As for the preparation of *gem*-dibromides, the treatment of 1,1-bis(trifluoromethanesulfonyloxy)alkanes with magnesium bromide-titanium(IV) chloride[12] and the cleavage of 1,3-benzodioxoles with boron tribromide[13] were investigated. These methods are, however, still problematic because they involve a multistep reaction route and hence the yields of halides are generally unsatisfactory. The Hunsdiecker reaction of α-halocarboxylic acids was also employed for the preparation of certain *gem*-dibromides.[14]

In the course of our continuous study on the oxidation of organic molecules with copper(II) compounds,[15] we found that the treatment of hydrazones of ketones and aldehydes **2** with copper(II) bromide-lithium *tert*-butoxide **3** gave *gem*-dibromides **4** in excellent yields (Scheme 1) [16] Recently it was also found that this reaction could be applied to the synthesis of corresponding *gem*-dichlorides **5**. We now report the full details of these preparations, including very much improved procedure using copper(II) halides-triethylamine.



RESULTS AND DISCUSSION

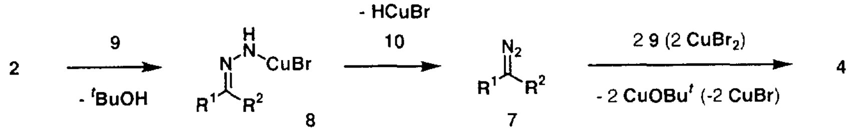
The preparation of hydrazones **2** is generally performed by the heating of ketones and aldehydes with excess hydrazines.[17] In such preparation, however, the formation of the corresponding azines is unavoidable. In fact the formation of azine by the treatment of hydrazone with water was reported,[18] and the preparation of hydrazone was successfully achieved by the treatment of azine with anhydrous hydrazine.[19] These observations suggest that hydrazones can be obtained without contamination of azines if the reaction of carbonyl compounds with hydrazine is carried out with continuous separation of water. Then we examined the preparation of hydrazones **2** by the treatment of carbonyl compounds **1** with hydrazine hydrate using molecular sieves as a dehydrating agent. The treatment of 4-phenylbutan-2-one **1a** with excess hydrazine hydrate (20 equiv) in methanol at rt for 2 h gave a mixture of the hydrazone **2a** and 4-phenylbutan-2-one azine (**6**) (**2a** : **6** = 63 : 37). On the other hand, as was expected, the formation of only a trace amount of **6** was observed by NMR spectrum of crude **2a** when the reaction was carried out in the presence of powdered molecular sieves 4 A (Scheme 2).[20] The similar treatments of ketones and aldehydes gave the corresponding hydrazones **2**, which were isolated by filtration and removal of volatile materials and employed for the further reaction without any purification.



The oxidation of hydrazones has been extensively studied as a method for the preparation of diazo compounds. A variety of reagents, such as lead(IV) acetate, mercury(II) oxide, mercury(II) trifluoroacetate, silver(I) oxide, manganese(IV) oxide, nickel peroxide, phenyldipyridinioiodine(III) bis(trifluoromethanesulfonate), and calcium hypochlorite, have been developed.[21] Since copper(II) bromide-lithium *tert*-butoxide **3** promotes 1,1-elimination of hydrogens,[15d] we expected that the treatment of hydrazones **2** with **3** gave the corresponding diazo compounds **7** or their degradation products. In fact, the treatment of 4-phenylbutan-2-one hydrazone (**2a**) with 4.4 equiv of the oxidizing agent **3** afforded 2,2-dibromo-4-phenylbutane (**4a**) in 61% yield (entry 1, Table 1). The first step of this reaction should be the formation of copper(II) amide **8** by the reaction of hydrazone **2** with *tert*-butoxycopper(II) bromide (**9**) which is the hypothetical active species in this oxidation. The intermediary diazo compound **7** would be formed by the α-elimination of copper(II) hydride **10**, which would react with another equivalent of **9** to form copper(I) bromide and *tert*-butanol. It is reasonable to assume that **4** was produced by the reaction of **7** with 2 equiv of **9** (Scheme 3). The yield of **4a** was largely improved by the use of an excess amount of oxidizing agent **3** (entry 2).

Since the second step of this reaction would be the oxidative halogenation of diazo compound **7** and should be effected also with copper(II) bromide,[22] we examined the combined use of 6 equiv of copper(II) bromide and 3 equiv of lithium *tert*-butoxide for the transformation of **2a** and found that **4a** was obtained in almost the same yield (entry 3). In a similar manner, various *gem*-dibromides **4** were obtained in good yields from hydrazones **2** prepared from aliphatic ketones and aldehydes. In the case of aromatic ketone, the corresponding *gem*-dibromide was not isolated. For example, the reaction of α-tetralone hydrazone **2h** gave the corresponding vinyl bromide **11**, and tetraphenylethylene **12** was isolated by the reaction of benzophenone hydrazone **2i** along with a small amount of benzophenone after aqueous work-up with NH_4OH.

$$CuBr_2 + LiOBu^t \longrightarrow \underset{\mathbf{9}}{BrCuOBu^t} + LiBr$$



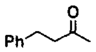
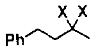
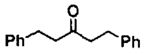
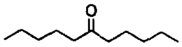
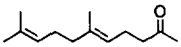
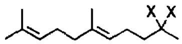
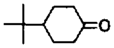
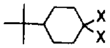
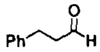
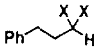
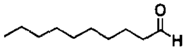
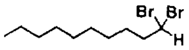
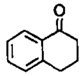
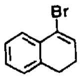
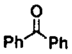
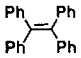
(3)

$$\mathbf{10} + \mathbf{9} \longrightarrow 2CuBr + {}^tBuOH$$

The present method was also applicable to the preparation of *gem*-dichlorides **5**. The treatment of acyclic ketone hydrazones **2** with 6 equiv of copper(II) chloride and 3 equiv of lithium *tert*-butoxide produced **5** in reasonable yields (entries 4 and 8). In the cases of 4-*tert*-butylcyclohexanone and hydrocinnamaldehyde hydrazones (**2e** and **f**), however, the yields were unsatisfactory as compared with the corresponding bromides **4** (entries 10 and 12).

The above method would be the first practical way for the preparation of *gem*-dibromides **4** and has a wide range of application. Then we further tried to improve the procedure for the oxidation of hydrazone **2**. The only drawback to the copper(II) bromide-lithium *tert*-butoxide procedure is the use of butyllithium which is expensive and requires the special care in handling. As shown in Scheme 3, the first step of the oxidation of hydrazone **2** would be the formation of copper(II) amide **8**. Since the acidity of the N-H bond in **2** is increased by the coordination of copper(II) salt to nitrogen atom, we expected that weak bases such as certain amines could remove a proton from the copper(II) complex **13** to form the amide **8** (Scheme 4). Then we examined the preparation of *gem*-dihalides **4** and **5** using the combination of copper(II) halides and amines.

Table 1. The Reaction of Hydrazones **2** with Copper(II) Halides - LiOBu^t.

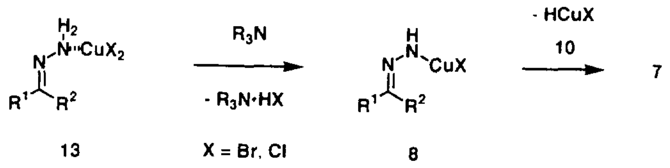
Entry	Ketone or Aldehyde **1**	Preparation of **2**[a]		CuX_2 (equiv)	LiOBu^t	Product	Overall Yield[b]	
		Temp °C	Time h		equiv			%
1		rt	2	$CuBr_2$ (4.4)	4.4		**4a**	61
2				$CuBr_2$ (6)	6			80
3	**1a**			$CuBr_2$ (6)	3	(X = Br)		82
4	**1a**			$CuCl_2$ (6)	3	(X = Cl)	**5a**	75
5	 **1b**	rt	2	$CuBr_2$ (6)	3		**4b**	83
6	 **1c**	rt	2	$CuBr_2$ (6)	3		**4c**	73
7	 *E* : *Z* = 60 : 40[c] **1d**	rt	1.5	$CuBr_2$ (6)	3	 (X = Br) *E* : *Z* = 6 : 4[d]	**4d**	81
8	**1d**			$CuCl_2$ (6)	3	(X = Cl) *E* : *Z* = 6 : 4[d]	**5d**	82
9	 **1e**	reflux	6	$CuBr_2$ (6)	3	 (X = Br)	**4e**	69
10	**1e**			$CuCl_2$ (6)	3	(X = Cl)	**5e**	48
11	 **1f**	rt	1	$CuBr_2$ (6)	3	 (X = Br)	**4f**	70
12	**1f**			$CuCl_2$ (6)	3	(X = Cl)	**5f**	55
13	 **1g**	rt	2.5	$CuBr_2$ (6)	3		**4g**	75
14	 **1h**	rt	24	$CuBr_2$ (6)	3		**11**	79
15	 **1i**	reflux	21	$CuBr_2$ (6)	3		**12**	63

a) Methanol was used as a solvent. b) Based on the carbonyl compound **1** used. c) Determined by capillary GLC analysis (SUPELCOWAX 10). d) Determined by ^1H (500 MHz) NMR spectrum.

Table 2. The Reaction of Hydrazones **2** with Copper(II) Bromide - Amines.

Entry	**2**	Amine (equiv)	$CuBr_2$ equiv	Solvent	Temp °C	Time h	Product	Overall Yield[a)] %
1	**2a**	Et_3N (6)	6	MeOH	rt	1	**4a**	79
2	**2a**	Et_3N (3)	6	MeOH	rt	0.5	**4a**	75
3	**2a**	Et_3N (3)	6	MeOH	rt	1	**4a**	79
4	**2a**	Et_3N (2.2)	4.4	MeOH	rt	0.5	**4a**	67
5	**2a**	Et_3N (4)	8	MeOH	rt	1	**4a**	78
6	**2a**	Et_3N (3)	6	DMF	rt	overnight	**4a**	trace
7	**2a**	Et_3N (3)	6	THF	rt	1	**4a**	trace
8	**2a**	Et_3N (3)	6	*t*-BuOH	rt	1	**4a**	-
9	**2a**	Bu_3N (6)	6	MeOH	rt	1	**4a**	59
10	**2a**	TMEDA[b)] (6)	6	MeOH	rt	1	**4a**	16
11	**2a**	DBU[c)] (6)	6	MeOH	rt	1	**4a**	30
12	**2a**	DABCO[d)] (6)	6	MeOH	rt	1	**4a**	36
13	**2a**	pyrrolidine (6)	6	MeOH	rt	1	**4a**	75
14	**2a**	morpholine (6)	6	MeOH	rt	1	**4a**	48
15	**2a**	Et_2NH (6)	6	MeOH	rt	1	**4a**	55
16	**2a**	$PhNMe_2$ (6)	6	MeOH	rt	1	**4a**	-
17	**2a**	-	6	MeOH	rt	1	**4a**	28
18	**2a**	-	6	THF	rt	1	**4a**	4
19	**2f**	Et_3N (3)	6	MeOH	rt	1	**4f**	62
20	**2f**	Et_3N (3)	6	MeOH	0	1	**4f**	73

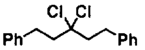
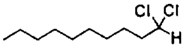
a) Based on the carbonyl compound **1** used. b) *N,N,N',N'*-Tetramethylethylenediamine. c) 1,8-Diazabicyclo[5.4.0]undec-7-ene. d) 1,4-Diazabicyclo[2.2.2]octane.



(4)

$$10 + R_3N{\cdot}CuX_2 \longrightarrow 2\,CuX + R_3N{\cdot}HX$$

Table 3. The Reaction of Hydrazones **2** with Copper(II) Halides - Et_3N.

Entry	**2**	CuX_2	Product	Overall Yield [a) %]	Entry	**2**	CuX_2	Product	Overall Yield[a) %]
1	**2a**	$CuBr_2$	**4a**	79	7	**2d**	$CuBr_2$	**4d**[c)]	82
2	**2a**	$CuCl_2$	**5a**	78	8	**2d**	$CuCl_2$	**5d**[c)]	78
3[b)]	**2b**	$CuBr_2$	**4b**	76	9	**2e**	$CuBr_2$	**4e**	64
					10	**2e**	$CuCl_2$	**5e**	56
4	**2b**	$CuCl_2$		80	11	**2f**	$CuBr_2$	**4f**	73
			5b		12	**2f**	$CuCl_2$	**5f**	67
5	**2c**	$CuBr_2$	**4c**	72	13	**2g**	$CuBr_2$	**4g**	74
6	**2c**	$CuCl_2$		70	14	**2g**	$CuCl_2$		63
			5c					**5g**	

a) Based on the carbonyl compound **1** used. b) Triethylamine (4 equiv) and copper(II) bromide (8 equiv) were used. c) *E* : *Z* = 6 : 4. The ratio was determined by ^1H (500 MHz) NMR spectrum.

As was expected, the treatment of hydrazone **2a** with 6 equiv of copper(II) bromide and more than 3 equiv of triethylamine in methanol gave the *gem*-dibromide **4a** in a good yield (see entries 1-5, Table 2). The reaction in dipolar, aprotic solvents such as THF or DMF gave only a trace amount of **4a**, which may be due to the poor solubility of copper(II) bromide in such solvents (entries 6 and 7). Among the various amines examined, triethylamine and pyrrolidine were found to be good choices though the reason is not clear at present. When *N*,*N*-dimethylaniline was employed, a substantial amount of insoluble material was precipitated, and the formation of **4a** was not observed. A considerable amount of **4a** was obtained by the reaction carried out in the absence of amine (entry 17), in which the hydrazone **2a** itself would serve as a base. In the case of the transformation of **2f**, the reaction temperature employed exerted an influence on the yield of *gem*-dibromide **4f** (see entries 19 and 20).

Based on these results, the reaction of various hydrazones **2** prepared from aliphatic ketones and aldehydes with copper(II) bromide (6 equiv) and triethylamine (3 equiv) was performed in methanol at 0 °C. The results listed in Table 3 indicate that *gem*-dibromides were obtained in the yields which were comparable to that obtained by the copper(II) bromide-lithium *tert*-butoxide procedure. In a similar manner, *gem*-dichlorides were also obtained by the treatment of **2** with copper(II) chloride in the presence of triethylamine. This procedure is clearly superior to the reaction using copper(II) chloride-lithium *tert*-butoxide in all respects including the yield of products.

CONCLUSION

It should be noted that the treatment of ketones and aldehydes with hydrazine hydrate in the presence of molecular sieves 4A and following reaction of the resulting crude hydrazones with copper(II) halides-triethylamine offer the convenient method for the preparation of *gem*-dibromides and chlorides with advantage of simplicity, safety, and inexpensiveness.

EXPERIMENTAL SECTION

General. All the reactions were carried out in a dry reaction vessel under argon. All melting points were determined with a Yanaco MP-S3 micromelting point apparatus. ^{1}H NMR spectra were measured for a $CDCl_3$ solution on Jeol FX-200 and Jeol ALPHA-500 instruments and are reported in parts per million from internal tetramethylsilane. IR spectra were recorded on a Jeol Diamond-20 FT-IR spectrometer; absorptions are reported in cm^{-1}. Elemental analyses were performed by Perkin Elmer 2400II. GLC analysis was carried out on a Shimadzu GC-7AG.

Materials. THF was distilled from benzophenone ketyl under argon immediately before use. Methanol was dried by the reaction with sodium, refluxed for several hours, distilled, and stored over molecular sieves 3A. Copper(II) halides were dried under vacuum (7-8 Torr) at 80 °C for 4 h. All ketones, aldehydes, and amines were either distilled or recrystallized before use.

A Typical Procedure: Preparation of 4-Phenyl-2-butanone Hydrazone (2a). Finely powdered molecular sieves 4A (1 g) was placed in a flask. Methanol (5 ml) and hydrazine hydrate (0.97 ml, 20 mmol) were added successively with stirring. After 20 min, a methanol (5 ml) solution of 4-phenyl-2-butanone (**1a**) (148 mg, 1 mmol) was added dropwise to the reaction mixture and the mixture was stirred for 2 h. Molecular sieves were filtered off and washed with ether. The filtrate was concentrated under reduced pressure and the excess hydrazine was further removed from the residue under vacuum (7-8 Torr) with gentle heating (30 °C) and stirring over 20 min to give the crude **2a**.

In a similar manner, the crude hydrazones **2b-i** were prepared and employed for further reactions.

A Typical Procedure: The Transformation of 4-Phenyl-2-butanone Hydrazone (2a) to 2,2-Dibromo-4-phenylbutane (4a) Using Copper(II) Bromide-LiOBu^t. To a THF solution of *tert*-butanol (6.2 ml, 3 mmol) was added a hexane solution of butyllithium (1.8 ml, 3 mmol) at 0 °C and the reaction mixture was stirred for 5 min. Copper(II) bromide (1.34 g, 6 mmol) was added to the mixture. The cooling bath was removed and stirring was continued for 20 min to give a dark brown solution. A THF (3 ml) solution of crude **2a** prepared from **1a** (1 mmol) was added dropwise over 5 min to the reaction mixture. Gentle evolution of nitrogen was observed during the addition. After being stirred for 1 h, the reaction was quenched by addition of 3.5% NH_3 aqueous solution. The organic materials were extracted with CH_2Cl_2, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to give **4a** (238 mg, 82%).

A Typical Procedure: The Transformation of 4-Phenyl-2-butanone Hydrazone (2a) to 2,2-Dichloro-4-phenylbutane (5a) Using Copper(II) Chloride-Triethylamine. To a methanol (6 ml) solution of copper(II) chloride (807 mg, 6 mmol) was added triethylamine (0.42 ml, 3 mmol) at 20 °C and the reaction mixture was stirred for 10 min at the same temperature. The mixture was cooled to 0 °C and a methanol (3 ml) solution of **2a** prepared from **1a** (1 mmol) was added dropwise over 10 min. Gentle evolution of nitrogen was observed during the addition. The cooling bath was removed and stirring was continued for 1 h. The reaction was quenched by addition of 3.5% NH_3 aqueous solution and organic materials were extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to give **5a** (159 mg, 78%).

The Physical Properties of *gem*-Dibromides 4. 2,2-Dibromo-4-phenylbutane (4a): IR (neat) 3030, 1604, 1496, 1055, 748, 698, 652, 580; ^{1}H NMR δ 7.38-7.16 (m, 5 H), 3.09-2.98 (m, 2 H), 2.58 (s, 3 H), 2.66-2.56 (m, 2 H). Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14. Found: C, 41.15; H, 4.18.

3,3-Dibromo-1,5-diphenylpentane (4b): mp 68.2-68.7 °C; IR (KBr) 3028, 1603, 1498, 1454, 1194, 1032, 756, 735, 702, 654, 580; ^1H NMR δ 7.39-7.17 (m, 10 H), 3.14-2.99 (m, 4 H), 2.75-2.61 (m, 4 H). Anal. Calcd for $C_{17}H_{18}Br_2$: C, 53.43; H, 4.75. Found: C, 53.21; H, 4.77.

6,6-Dibromoundecane (4c): IR (neat) 2956, 2933, 2871, 2862, 1466, 1379, 727, 646, 577, 551; ^1H NMR δ 2.39-2.27 (m, 4 H), 1.78-1.58 (m, 4 H), 1.47-1.26 (m, 8 H), 0.92 (t, J = 6.7 Hz, 6 H). Anal. Calcd for $C_{11}H_{22}Br_2$: C, 42.06; H, 7.06. Found: C, 42.34; H, 7.25.

2,2-Dibromo-6,10-dimethylundeca-5,9-diene (4d): IR (neat) 2968, 2924, 2856, 1446, 1377, 1165, 1074, 1061, 833, 650, 584; ^1H NMR δ 5.22-5.04 (m, 2 H), 2.54 (s, 1.8 H), 2.53 (s, 1.2 H), 2.43-2.29 (m, 4 H), 2.12-1.96 (m, 4 H), 1.71 (d, J = 0.9 Hz, 1.2 H), 1.70 (s, 1.2 H), 1.69 (d, J = 0.9 Hz, 1.8 H), 1.66 (s, 1.8 H), 1.62 (s, 1.2 H), 1.61 (s, 1.8 H). Anal. Calcd for $C_{13}H_{22}Br_2$: C, 46.18; H, 6.56. Found: C, 46.15; H, 6.39.

1,1-Dibromo-4-*tert*-butylcyclohexane (4e): IR (neat) 2956, 2868, 1442, 1394, 1367, 1182, 1097, 1014, 999, 825, 773, 710, 546, 505; ^1H NMR δ 2.80-2.71 (m, 2 H), 2.38-2.28 (m, 2 H), 1.67-1.51 (m, 4 H), 1.11 (tt, J = 11.1, 4.3 Hz, 1 H), 0.87 (s, 9 H). Anal. Calcd for $C_{10}H_{18}Br_2$: C, 40.30; H, 6.09. Found: C, 40.36; H, 6.08.

1,1-Dibromo-3-phenylpropane (4f): IR (neat) 3030, 1604, 1496, 1456, 1161, 750, 700, 677, 602, 588, 567, 553; ^1H NMR δ 7.39-7.12 (m, 5 H), 5.57 (t, J = 6.1 Hz, 1 H), 2.90-2.76 (m, 2 H), 2.76-2.61 (m, 2 H). Anal. Calcd for $C_9H_{10}Br_2$: C, 38.89; H, 3.63. Found: C, 39.17; H, 3.87.

1,1-Dibromodecane (4g): IR (neat) 2960, 2925, 2856, 1466, 1379, 1157, 675, 602, 571; ^1H NMR δ 5.71 (t, J = 6.2 Hz, 1 H), 2.48-2.31 (m, 2 H), 1.64-1.44 (m, 2 H), 1.44-1.13 (m, 12 H), 0.89 (t, J = 6.5 Hz, 3 H). Anal. Calcd for $C_{10}H_{20}Br_2$: C, 40.03; H, 6.72. Found: C, 40.16; H, 6.66.

The Physical Properties of *gem*-Dichlorides 5. 2,2-Dichloro-4-phenylbutane (5a): IR (neat) 3028, 1603, 1498, 1454, 1059, 750, 700, 646, 609, 550; ^1H NMR δ 7.37-7.16 (m, 5 H), 3.07-2.92 (m, 2 H), 2.57-2.43 (m, 2 H), 2.20 (s, 3 H). Anal. Calcd for $C_{10}H_{12}Cl_2$: C, 59.14; H, 5.95. Found: C, 59.48; H, 6.10.

3,3-Dichloro-1,5-diphenylpentane (5b): mp 40.5-41.0 °C; IR (KBr) 3028, 1603, 1498, 1454, 1032, 750, 700, 679, 507, 501; ^1H NMR δ 7.38-7.16 (m, 10 H), 3.08-2.91 (m, 4 H), 2.63-2.46 (m, 4 H). Anal. Calcd for $C_{17}H_{18}Cl_2$: C, 69.63; H, 6.19. Found: C, 69.77; H, 6.22.

6,6-Dichloroundecane (5c): IR (neat) 2956, 2933, 2875, 2873, 1468, 1381, 737, 729, 687, 640, 600; ^1H NMR δ 2.25-2.10 (m, 4 H), 1.74-1.45 (m, 4 H), 1.45-1.23 (m, 8 H), 0.92 (t, J = 6.6 Hz, 6 H). Anal. Calcd for $C_{11}H_{22}Cl_2$: C, 58.67; H, 9.85. Found: C, 58.99; H, 10.01.

2,2-Dichloro-6,10-dimethylundeca-5,9-diene (5d): IR (neat) 2968, 2929, 2856, 1444, 1379, 1169, 1080, 1070, 833, 694, 646, 602; ^1H NMR δ 5.18-5.05 (m, 2 H), 2.43-2.31 (m, 2 H), 2.25-2.18 (m, 2 H), 2.16 (s, 1.8 H), 2.15 (s, 1.2 H), 2.11-1.96 (m, 4 H), 1.70 (d, J = 1.2 Hz, 1.2 H), 1.69 (s, 1.2 H), 1.68 (d, J = 1.1 Hz, 1.8 H), 1.64 (s, 1.8 H), 1.61 (s, 1.2 H), 1.60 (s, 1.8 H). Anal. Calcd for $C_{13}H_{22}Cl_2$: C, 62.65; H, 8.90. Found: C, 63.05; H, 8.96.

1,1-Dichloro-4-*tert*-butylcyclohexane (5e): IR (neat) 2960, 2871, 1446, 1396, 1367, 1186, 1103, 1018, 1003, 897, 835, 783, 733, 579; ^1H NMR δ 2.61-2.51 (m, 2 H), 2.07-2.17 (m, 2 H), 1.75-1.67 (m, 2 H), 1.46-1.57 (m, 2 H), 1.07 (tt, J = 12.4, 3.4 Hz, 1 H), 0.87 (s, 9 H). Anal. Calcd for $C_{10}H_{18}Cl_2$: C, 57.43; H, 8.67. Found: C, 57.90; H, 8.87.

1,1-Dichloro-3-phenylpropane (5f): IR (neat) 3030, 1604, 1498, 1456, 1230, 787, 752, 700, 677, 658, 571, 505; ^{1}H NMR δ 7.35-7.29 (m, 2 H), 7.25-7.18 (m, 3 H), 5.66 (t, *J* = 6.1 Hz, 1 H), 2.88 (t, *J* = 7.5 Hz, 2 H), 2.51 (dt, *J* = 7.5, 6.1 Hz, 2 H). Anal. Calcd for $C_9H_{10}Cl_2$: C, 57.17; H, 5.33. Found: C, 56.92; H, 5.42.

1,1-Dichlorodecane (5g): IR (neat) 2956, 2925, 2856, 1466, 1223, 748, 679, 660; ^{1}H NMR δ 5.74 (t, *J* = 6.1 Hz, 1 H), 2.27-2.12 (m, 2 H), 1.66-1.44 (m, 2 H), 1.44-1.15 (m, 12 H), 0.88 (t, *J* = 6.3 Hz, 3 H). Anal. Calcd for $C_{10}H_{20}Cl_2$: C, 56.88; H, 9.55. Found: C, 57.03; H, 9.55.

The Physical Properties of 1-Bromo-3,4-dihydronaphthalene (11): IR (neat) 3018, 2935, 2885, 2829, 1616, 1479, 1448, 1425, 1317, 1277, 949, 833, 756, 729, 690; ^{1}H NMR δ 7.56-7.50 (m, 1H), 7.25-7.12 (m, 2H), 7.08-7.00 (m, 1H), 6.40 (t, *J* = 4.9 Hz, 1H), 2.79 (t, *J* = 8.1 Hz, 2H), 2.32 (dt, *J* = 8.1, 4.9 Hz, 2H). Anal. Calcd for $C_{10}H_9Br$: C, 57.45; H, 4.34. Found: C, 57.37; H, 4.28.

The Physical Property of Tetraphenylethylene (12): mp 228-229 °C (lit.[23]) mp 225 °C).

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20. The physical properties of **6**: mp 47.0-47.5 °C; IR (KBr) 3022, 2956, 1637, 1494, 1450, 754, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.32-7.09 (m, 10 H), 2.96-2.84 (m, 3 H), 2.79-2.65 (m, 1 H), 2.65-2.50 (m, 4 H), 2.12 (s, 0.4 H), 1.97 (s, 1.3 H), 1.73 (s, 1.1 H), 1.66 (s, 3.2 H). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.29; H, 8.32; N, 9.42. The spectral data of the crude **2a** were as follows; IR (neat) 3365, 3215, 3026, 2927, 1647, 1618, 1603, 1496, 1454, 1367, 804, 748, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.32-7.11 (m, 5 H), 4.98-4.80 (m, 1.3 H), 4.80-4.65 (m, 0.7 H), 2.86-2.75 (m, 2 H), 2.54-2.41 (m, 2 H), 1.87 (s, 1 H), 1.73 (s, 2 H).

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