

## Dehydrohalogenation of *vic*-Dihaloalkanes over Silica Gel

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Received April 9, 1985

The use of silica gel and other solids with active surfaces as catalysts for gas-phase dehydrohalogenation at high temperatures (200–500 °C) is well-known. An E<sub>1</sub> or like E<sub>1</sub> mechanism is generally accepted for reactions over silica gel.<sup>2</sup> By contrast, there is little information about reactions performed in solution.

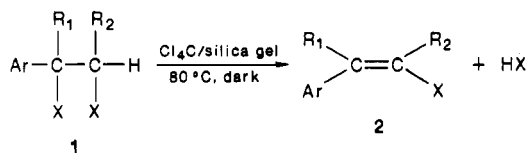
Incremona and Martin<sup>3</sup> reported the 2d formation (56% yield) by passing 1d through a column of Fluorosil with carbon tetrachloride as eluent and Kato et al.<sup>4</sup> reported the dehydrochlorination of cembrene derivatives on silica gel plates, at room temperature. Nevertheless, as far as we know this reaction has not been systematically studied.

The present paper describes the behavior of the 1,2-dihaloalkanes 1a–r in carbon tetrachloride solutions added with commercially available silica gel and heated at 80 °C in the dark. Table I summarizes structural changes in 1. In the case of 1,1-diaryl-substituted dihalides 1a–i, this reaction resulted in a mild, simple, and extremely convenient method for effective dehydrohalogenation (Scheme I).

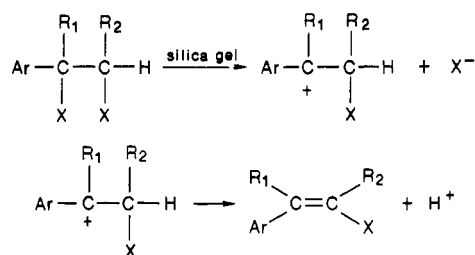
Filtration and rotary evaporation of the solutions directly provided the corresponding vinylic products 2a–i in high yield and usually in excellent purity (see Table II). A series of control reactions were performed under similar conditions but without adding silica gel. The conversion of the dihaloalkanes was estimated by <sup>1</sup>H NMR and the results are also collected in Table II. The dihalides 1j–k were very reactive and gave complete thermal dehydrohalogenation in a few minutes, so the catalytic effect of silica gel could not be demonstrated. The reactivity of compounds 1a–i agrees with the proposed cationic mechanism initiated by loss of the tertiary halide atom<sup>2</sup> (Scheme II).

Although most of the compounds 2a–i have been prepared by other methods,<sup>5–15</sup> the synthetic procedure described here gave more than 95% of vinylic product and these results are generally better than those previously reported. The exceptions were compound 1b that yielded 40% of the vinylic dibromide 2b in a complex mixture with

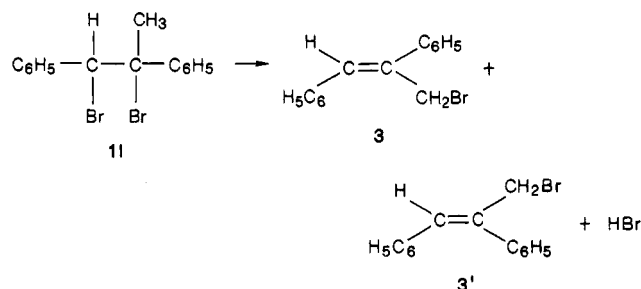
Scheme I



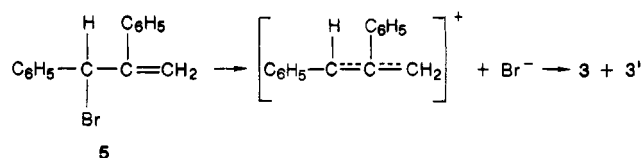
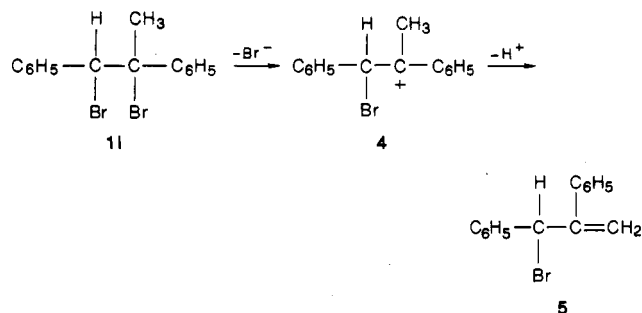
Scheme II



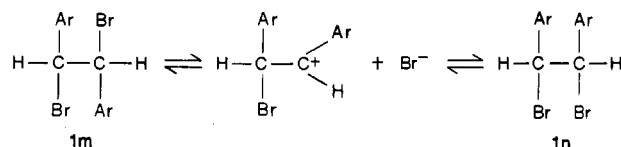
Scheme III



Scheme IV



Scheme V



1b and 1a and compound 1f which led to a maximum of 50% of conversion in 12 h. The less hindered substrates 1l–n did not give the vinylic derivatives but some of them gave another type of product. In connection with this last group of reagents, the most interesting result was obtained with compound 11, the *erythro*-1,2-dibromo-1,2-diphenylpropane, which yielded a mixture of isomeric allylic halides 3 and 3' that cannot be produced by vicinal dehydrohalogenation (Scheme III).

One of the referees suggested to us a mechanism for this reaction initiated by the loss of a bromide ion at the silica

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Table I. *vic*-Dihaloalkanes 1a-r

1	Ar	R <sub>1</sub>	R <sub>2</sub>	X
a	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	Br
b	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Br	Br
c	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Cl
d	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Br
e	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	Br
f	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Cl
g	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Br
h	<i>p</i> -H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	<i>p</i> -H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Cl
i	<i>p</i> -H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	<i>p</i> -H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Cl
j	<i>p</i> -H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	<i>p</i> -H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Br
k	<i>p</i> -H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	<i>p</i> -H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Br
l (erythro)	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	Br
m ( <i>d,l</i> )	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	Br
n (meso)	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	Br
o	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	Cl
p	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	Br
q	<i>p</i> -H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	Cl
r	<i>p</i> -H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	Br

Table II. Dehydrohalogenation of *vic*-Dihaloalkanes<sup>a</sup>

sub- strate	prod- uct	reactions conditions				
		A			B	
		<i>t</i> (min)	% convn	% yield	<i>t</i> (min)	% convn
1a	2a	60	100	96	60	NR
1b	2b	30	40		30	NR
1c	2c	480	96	87	480	11
1d	2d	35	98	95	35	14
1e	2e	30	100	94	30	43
1f	2f	720	50	37	720	12
1g	2g	720	96	91	720	25
1h	2h	300	100	81	300	40
1i	2i	15	100	95	15	58
1j	2j	10	100	93	10	100
1k	2k				5	100
1l	3 + 3'	120	83		120	NR
1m	1n	720	100	98	720	10
1n		720	NR		720	NR

<sup>a</sup>A = reactions carried out with silica gel. B = reactions performed without silica gel. *t* = time in minutes. NR = no reaction. convn = % conversion of 1 by <sup>1</sup>H NMR. yield = % of pure products.

surface (Scheme IV). The tertiary carbocation 4 would lead to a Hofmann product, 5. The formation of a Hofmann product by E<sub>1</sub> elimination from 1,2-diphenyl-1-X-propanes has been previously reported.<sup>16</sup> Isomerization of 5 to the more stable products 3 and 3' would occur at the acidic surface of silica gel.

Compound 1m isomerized to the meso isomer 1n but the reverse reaction, 1n → 1m, did not take place. In the first step of 1m isomerization, the loss of a halide ion by action of the silica gel giving a cationic intermediate could be postulated. The same secondary cationic intermediate could be formed from 1n, so there are no mechanistic reasons for the lack of reactivity of the "meso" isomer (Scheme V).

The insolubility of 1n in carbon tetrachloride would favor the total 1m isomerization by equilibrium displacement to the insoluble isomer. Similar reasons could also explain the lack of 1m formation from 1n. On the other hand, the insolubility of 1n would make difficult the contact between active sites on silica gel surface and the molecules of the reagent. Thus, 1n remained unchanged, still after prolonged treatment with silica gel.

Reactions of 1,1-asymmetrically substituted compounds 1o-r gave results that were also consistent with the participation of carbenium ions. Equimolar mixtures of *E*-Z

isomers were obtained from the dihalides 1q-r. The dehydrohalogenation products of 1o,p underwent further isomerization at the silica surface and the *Z* isomers predominated (Table III). Finally, the dibromo and dichloro derivatives of 1-phenylethane and 1-phenylpropane were unreactive under these conditions. The secondary carbonium intermediate should be unstable and would react immediately with the halide ion. The experiments were all carried out in the dark because the 1,1-diaryl-1,2-dibromoalkanes in carbon tetrachloride solutions are photosensitive, giving bromine elimination as we reported in a previous work.<sup>20</sup>

## Experimental Section

Melting points were determined in closed capillary tubes and were uncorrected. Microanalyses were performed on a F and M 185 microcombustion apparatus. Halogen contents were determined by volumetric titration with a Seybold Digital GTE potentiometer. <sup>1</sup>H NMR spectra were recorded on a T-60 Varian spectrometer with tetramethylsilane as internal standard and carbon tetrachloride as solvent. Mass spectra were performed at 70 eV on a Finnigan 3300, F-100 spectrometer coupled with a 1500 INCOS computer. The silica gel used as catalyst was Kieselgel 60 (Merck) for column chromatography activated at 105 °C. The 1,2-dihaloalkanes were synthesized by halogen addition to a solution of the corresponding alkenes in carbon tetrachloride at -15 °C in the dark. Aliquots of the resulting solutions of compounds 1a-k and 1o-r were checked by <sup>1</sup>H NMR in order to verify their complete halogenation. The dihalides 1l-n were isolated and purified by different methods. Physical data agree with those present in the literature.

### General Procedure for Dehydrohalogenation Reactions.

To a solution of 1 (5 mmol) in carbon tetrachloride was added a variable amount (5-20 mg) of silica gel. The reaction flask was covered with aluminum foil, immersed in a water bath at 80 °C, and gently refluxed. Upon completion, the mixture was filtered and the silica gel washed thoroughly with fresh carbon tetrachloride. The filtrate and the washing were combined and the solvent was removed in vacuo. The residual products were recrystallized or distilled when necessary and then identified by usual physical data: melting point or boiling point, <sup>1</sup>H NMR, MS, and IR.

As compound 1n is insoluble in carbon tetrachloride, suspensions of 1n and silica gel were vigorously stirred while refluxed. In order to separate 1n from the silica gel at the end of the reaction, the solvent was vacuum evaporated and the remaining solid was several times extracted with boiling ethanol. After filtration, the solvent was distilled under reduced pressure and pure 1n was obtained. The following data have not been previously reported in the literature.

**2-Chloro-1,1-bis(*p*-chlorophenyl)propene (2f).** The crude product was chromatographed on alumina with *n*-hexane as eluent and then recrystallized from methanol, giving a white solid: mp 80.5-81 °C; <sup>1</sup>H NMR δ 2.30 (3 H, s), 6.92-7.39 (8 H, m); MS (70 eV) (*m/e*, relative intensity) 302 (0.5) (M<sup>+</sup>), 300 (1.6) (M<sup>+</sup>), 296 (4.3) (M<sup>+</sup>), 151 (30), 149 (80.4). Anal. Calcd: C, 60.53; H, 3.72; Cl, 35.74. Found: C, 60.47; H, 3.58; Cl, 35.90.

**2-Chloro-1,1-bis(*p*-methylphenyl)propene (2h).** In the literature 2h is mentioned as a white solid, mp 43-43.5 °C,<sup>15</sup> but we were unable to crystallize the pale yellow oil obtained from the reaction. Several attempts were made of recrystallization with different solvents and the samples were also chromatographed on alumina with *n*-hexane as eluent. The analytical data agree well with the proposed structure and have not been previously reported: <sup>1</sup>H NMR δ 2.17 (3 H, s), 2.24 (6 H, s), 6.85-7.25 (8 H, m); MS (70 eV) (*m/e*, relative intensity) 258 (12) (M<sup>+</sup>), 256 (28)

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Table III. Dehydrohalogenation of *vic*-Dihaloalkanes over Silica Gel

substrate	products	<i>t</i> (min)	yield by <sup>1</sup> H NMR	
			<i>Z</i>	<i>E</i>
1o	( <i>Z</i> )-2o and ( <i>E</i> )-2o	5	40	30
1o	( <i>Z</i> )-2o and ( <i>E</i> )-2o	60	57	33
1o	( <i>Z</i> )-2o and ( <i>E</i> )-2o	90	76	23
1p	( <i>Z</i> )-2p and ( <i>E</i> )-2p	10	57	17
1p	( <i>Z</i> )-2p and ( <i>E</i> )-2p	20	82	18
1p	( <i>Z</i> )-2p and ( <i>E</i> )-2p	60	90	10
1q	( <i>Z</i> )-2q and ( <i>E</i> )-2q	10	~50	~50
1r	( <i>Z</i> )-2r and ( <i>E</i> )-2r	5	~50	~50

(M<sup>+</sup>), 129 (100). Anal. Calcd: C, 79.52; H, 6.67; Cl, 13.81. Found: C, 79.38; H, 6.60; Cl, 13.92.

**2-Bromo-1,1-bis(*p*-methylphenyl)propene (2j).** The crude product was recrystallized from methanol, giving a white solid: mp 67–68 °C; <sup>1</sup>H NMR δ 2.27 (3 H, s), 2.34 (3 H, s), 2.37 (3 H, s), 6.88–7.35 (8 H, m); MS (70 eV) (*m/e*, relative intensity) 302 (4.2) (M<sup>+</sup>), 300 (4.3) (M<sup>+</sup>), 129 (100). Anal. Calcd: C, 67.78; H, 5.69; Br, 26.53. Found: C, 67.60; H, 5.48; Br, 26.90.

**Reactions of 1,1-Asymmetrically Substituted Compounds 1o–r.** Only the *Z* isomers of 2o,p and the *E* isomers of 2q,r could be isolated. After purification by column chromatography and recrystallization they were identified as described.<sup>17–19</sup> Elemental analyses, <sup>1</sup>H NMR, and mass spectra of the reaction mixtures were performed and compared with those of the pure isolated products. The results obtained show the presence of *E*–*Z* mixtures (Table III).

**(*E*)-2-Bromo-1-(4-methylphenyl)-1-phenylethene (2r).** This compound is described as a liquid in the literature;<sup>18</sup> we have obtained it as a solid: mp 56–57 °C (ethanol); <sup>1</sup>H NMR (Cl<sub>4</sub>C) δ 2.35 (3 H, s), 6.62 (1 H, s), 6.92–7.40 (9 H, m); MS (70 eV) (*m/e*, relative intensity) 274 (100) (M<sup>+</sup>), 272 (97) (M<sup>+</sup>), 193 (60), 178 (65), 115 (75). Anal. Calcd: C, 65.85; H, 4.80; Br, 29.35. Found: C, 65.79; H, 4.92; Br, 29.95.

**(*Z*)-3-Bromo-1,2-diphenylpropene (3).** *erythro*-1,2-Dibromo-1,2-diphenylpropane (11) was synthesized, isolated, and identified as described.<sup>21</sup> At the end of the reaction with silica gel the solution was filtered and the solvent removed. The mixture of allylic halides 3 and 3' was analyzed by <sup>1</sup>H NMR spectroscopy and then vacuum distilled at 130–135 °C, 0.01 torr. Boiling point and analytical data agree with those in literature.<sup>22</sup> <sup>1</sup>H NMR δ 4.28 (2 H, s), 4.35 (2 H, br s), 6.61 (1 H, s), 6.77 (1 H, br s), 6.90–7.50 (10 H, m). The <sup>1</sup>H NMR spectra indicated that the isomers were formed in a 3/1 ratio. The distilled mixture was chromatographed through a column consisting of 15 g of silica gel placed over 105 g of alumina with *n*-hexane as eluent. As the halides decomposed only a minor amount of pure 3 was obtained as an oil. The *Z* geometry was assigned to the main product by comparing the <sup>1</sup>H NMR spectra of 3 and 3' with the signals of vinylic and aromatic protons in *cis*- and *trans*-stilbenes and (*E*)-1,2-diphenylpropene.

<sup>1</sup>H NMR of 3: δ 4.35 (2 H, br s, CH<sub>2</sub>Br), 6.77 (1 H, br s, C=CH), 6.90–7.50 (10 H, m, ArH); MS (25 eV) (*m/e*, relative intensity) 274 (3.5) (M<sup>+</sup>), 272 (3.7) (M<sup>+</sup>), 193 (45) (M<sup>+</sup> – Br), 192 (12) (M<sup>+</sup> – HBr) 115 (100) (M<sup>+</sup> – HBr – C<sub>6</sub>H<sub>5</sub>). Anal. Calcd: C, 65.95; H, 4.80. Found: C, 65.79; H, 4.70. Bromine was not titrated.

**Registry No.** 1a, 40957-21-9; 1b, 94611-18-4; 1c, 59856-01-8; 1d, 94611-16-2; 1e, 94611-17-3; 1f, 106403-85-4; 1g, 106403-86-5; 1h, 106403-87-6; 1i, 106403-88-7; 1j, 106403-89-8; 1k, 106403-90-1; 1l, 63904-71-2; 1m, 13027-48-0; 1n, 13440-24-9; 1o, 106403-91-2; 1p, 106403-92-3; 1q, 106403-93-4; 1r, 106403-94-5; 2a, 13249-58-6; 2b, 2592-73-6; 2c, 781-34-0; 2d, 781-32-8; 2e, 22133-88-6; 2f, 101414-10-2; 2g, 97193-00-5; 2h, 106403-95-6; 2i, 81360-98-7; 2j, 82357-51-5; 2k, 39179-87-8; (*Z*)-2o, 15725-99-2; (*E*)-2o, 15726-00-8; (*Z*)-2p, 99632-23-2; (*E*)-2p, 99632-31-2; (*Z*)-2q, 15726-03-1; (*E*)-2q, 15726-04-2; (*Z*)-2r, 106403-96-7; (*E*)-2r, 106403-97-8; 3, 106403-98-9; 3', 106403-99-0.

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## A Convenient Synthesis of C-Unsubstituted and C-Monoalkylated Ketene Imines by Dehydrocyanation of Imidoyl Cyanides Using Vacuum Gas–Solid Reactions

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Received April 7, 1986

Substituted ketene imines with at least one aromatic substituent on nitrogen or carbon are well-known and have been described extensively in the literature, especially in view of their potential to be used in cycloaddition reactions.<sup>1</sup> Specific synthetic approaches exist for the preparation of the parent compound,<sup>2</sup> the trisilylated analogue,<sup>3</sup> and the *N*-methyl<sup>4</sup> and *N*-*tert*-butyl<sup>5</sup> derivatives. Recently, a synthesis of trialkyl ketene imines using  $\alpha$ -halo imino chemistry via base-induced elimination of hydrogen cyanide from  $\alpha$ -cyano enamines was reported.<sup>6</sup> However, this method is not suitable for the preparation of less substituted ketene imines because of the difficulties in synthesizing the corresponding  $\alpha$ -cyano enamine precursors.

We report now that aliphatic  $\alpha$ -imidoyl cyanides are useful precursors for the general synthesis of the volatile C-unsubstituted and C-monosubstituted *N*-alkyl ketene imines by an appropriate dehydrocyanation using a vacuum gas–solid reaction (VGSR).<sup>7</sup>

### Results and Discussion

Stable aliphatic  $\alpha$ -imidoyl cyanides are accessible from *N*-chlorination/dehydrochlorination of  $\alpha$ -amino nitriles, but the reported reaction conditions (*t*-BuOCl/Et<sub>3</sub>N or DABCO)<sup>8</sup> are not compatible with the less substituted alkyl species (R<sup>1</sup> = H, Me; R = H, Me) due to extensive decomposition of the reaction products. However, by altering the reaction conditions, it was possible to synthesize these latter species in good yields (73–88%). The  $\alpha$ -(*N*-alkylamino) nitrile precursors 1 were prepared by a classical Strecker synthesis (87–98%) involving condensation of an aldehyde (R<sup>1</sup> = H, Me) with a primary amine (R = H, Me) (under hydrochloride form) in the presence of sodium cyanide in aqueous methanol at –30 °C (Scheme I).<sup>9</sup> The conversion of  $\alpha$ -amino nitriles 1 into  $\alpha$ -imino nitriles 2 was accomplished in 73% overall yield by *N*-chlorination with *N*-chlorosuccinimide (NCS) followed by dehydrochlorination with solid potassium hydroxide. Both reactions were performed at –30 °C in tetraglyme because the intermediate  $\alpha$ -(*N*-chloroamino) nitriles decompose violently (and often explosively!), even at 0 °C in solution. Hence, these labile *N*-chloroamino compounds were not isolated but immediately treated with a suspension of pulverized potassium hydroxide. The  $\alpha$ -imino nitriles 2 thus formed were separated from tetraglyme by distillation at reduced pressure (10<sup>–2</sup> torr). The water formed during the dehydrochlorination step is codistilled and finally separated by drying over molecular sieves. Imidoyl cyanides exist as the *Z* isomer exclusively (as evidenced by <sup>1</sup>H NMR analysis) except for the less substituted 2-(*N*-methylimino)propanenitrile 2a, which showed also the

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