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Solid-State Organic Reactions Proceeding by Pulverization: Oxidation and Halogenation with Iodosobenzene and Inorganic Solid-Supports.

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Abstract: Pulverization-activation method was employed to accelerate solid-state organic reactions. Crushing and grinding of solid mixtures of hydrogen halide-treated silica gels, iodosobenzene and organic substrates in the absence of a solvent brought about smooth and rapid reactions to give halogenated and/or oxidized products in good yields. Various sulfides were smoothly converted to sulfonyl chlorides in one step in excellent yields. The surface of silica gel activated by pulverization serves as a reaction field on which reagent molecules can effectively encounter with each other. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

There have been much interest in solid-state organic reactions because of their advantages such as faster reactions than in the presence of a solvent, characteristic selectivities different from those in solution, and environmentally friendliness without the use of a poisonous solvent.¹ Recently, Toda et al. developed photochemical reactions of new types of host-guest complexes proceeding with the remarkably selective stereochemical control.^{2, 3} For these reactions, however, adequate crystals or host-guest complexes must be prepared for the particular reactions, which hampers the general use of this type of reactions. As for activation methods, Bram et al. demonstrated the usefulness of microwave in the presence of inorganic supports without organic solvents.⁴ Substrates are adsorbed on inorganic supports such as alumina or montmorillonite and irradiated to give products in a short period. It has also become clear that when organic and inorganic polymers are mechanically pulverized, activated spots emerges on their surfaces. For example, pulverization of quartz produced hot spots and radical species on the crushed surface.⁵ If it is possible to utilize such activated spots,



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solid-state organic reactions must be much improved and become a general method of organic synthesis.

In preliminary studies,⁶ we reported a novel type of solid-state organic reactions proceeding by pulverization. As shown in scheme 1, five minutes' pulverization of the mixtures of iodosobenzene, hydrogen halide-treated silica gel, and organic substrates exhibited various types of reactions such as oxidation and halogenation in good yields.

Entry	Substrate ^a -	Products, Yield (%) ^b		
2		HCI-Silica gel	HBr-Silica gel	HI-Silica gel
1	Ph Ph	CI Ph Ph CI 65	Br Ph Ph Br 39	H >= O Ph 5<
2	Ph Ph	Cl Ph Ph Cl 58	Br Ph Ph Br 58	Ph Ph 36, no adducts
З	PhPh	Ph Ph 74	Br Ph Br 51	Ph Ph trace(6>)
4	Ph	Ph Cl HO Ph 80	HO HO Ph 27	HO Ph 41
5	Ph Ph Ph	CL Ph CL Ph OH Ph Ph 66	O Ph Ph 47	O Ph Ph 58
6		no reaction	no reaction	no reaction
7	Ph Ph Ph Ph	Ph O Ph Ph Ph 82	no reaction	no reaction
8	XX		Br Br	
		60	50	17

 Table 1. Solid-state Pulverization Reactions of Alkenes and an Alkyne with HX-Silica Gel and PhIO

^a Substrate: 100 mg, PhIO: 2.2eq (ca.150 mg-720 mg) for each alkenyl bond, HX-silica gel: 20 g.
 ^b Isolated yield.

In the above reactions, we successfully utilized a polymeric and insoluble reagent, iodosobenzene, without addition of a Lewis acid. Iodosobenzene is a hypervalent iodine compound and has become an increasingly popular reagent for promoting oxidation and other transformations.⁷⁻⁹

In the present article, we provide a full account of the experimental detail and propose most probable mechanisms of the reactions.

RESULTS AND DISCUSSION

Halogenation and oxidation of unsaturated compounds.

A mixture of silica gel saturated with a vapor of concd HCl, iodosobenzene, and a substrate was crushed and ground in a mortar for 5 min. Extraction with ether gave the products.

Table 1 summarizes typical results of the reaction of alkenes and an alkyne. It is clear that the reaction course and the yields of the products depend on the structure of the substrates and the kind of HX-silica gels (X=Cl, Br, or I) employed.

HCl-silica gel was reacted with 1,2-disubstituted alkenes and an alkyne (entries 1-3) to afford 1,2dichlorinated adducts in good yields. With HBr-silica gel, the same type of compounds were obtained but in lower yields, whereas with HI-silica gel the reaction hardly proceeded. These addition reactions were not

Entry	Substrate ^a	Product	Yield (%) ^b
1			31 ^c
2	\Box	CICI	31
3	OMe OMe OMe	Q.	79
4	OMe OMe OMe		42 52
5		recovered quantitatively	

 Table 2. Solid-state Pulverization Reactions of Aromatic Compounds with HCI-Silica Gel and PhIO

^a Substrate: 50 mg, PhIO: 4.4 eq. to the substrate, HCI-silica gel: 10 g.

Temp.: 200°C. Column Temp.: 70°C→200°C (32°C/min).

^b Isolated yields. ^c Determined by GLC. Column: OV-1 (2 %) 1.5m. Inj.

stereoselective. 1,1-Disubstituted and tri- and tetra-substituted alkenes¹⁰ (entries 4, 5, 7, 8) behaved differently from 1,2-disubstituted ones and gave interesting products as shown in Table 1. Halogenation did not occur at the disubstituted carbon atoms of alkenes. Cinnamic acid, one of tri-substituted alkenes, did not undergo the reaction (entry 6) suggesting that an electron-withdrawing carboxyl group interfered the reaction.

In order to evaluate the importance of adsorbed water on silica gel, a dry HCl-silica gel reagent was prepared with dry HCl gas. The reactions of the reagent with trans-stilbene and tetraphenyl ethylene were essentially the same as those with the wet reagent. It should also be emphasized that most substrates used are solid and the reaction is totally a solid system.

Aromatic compounds also gave halogenated and oxidized products as expected. Table 2 summarizes the results with HCl-silica gel; HBr and HI-silica gels were not reactive to give considerable amounts of products.

Anthracene,¹¹ acenaphthylene, and some other aromatic compounds having electron-donating substituents gave relatively selective oxidation / chlorination products in moderate yields (entries 1-4). On the other hand, an aromatic compound with electron-withdrawing substituents such as halogens was recovered quantitatively (entry 5). The reaction has a great advantage that it can be applied to hardly soluble aromatic compounds.

One-step synthesis of sulfonyl chlorides from sulfides.

A number of papers have been published on the synthesis of sulfonyl chlorides from sulfides using a variety of reaction procedures with different types of chlorinating reagents. Chlorine gas in aqueous acetic acid has been the most well-known method.¹² However, the use of chlorine gas is tedious and quite often causes a trouble. The present method gives comparable or better reaction yields to the chlorine gas method with a much easier manipulation.¹³

As summarized in Table 3, sulfides bearing at least one benzylic C-S bond such as dibenzyl, alkyl benzyl, and benzyl phenyl sulfides were converted into the corresponding sulfonyl chlorides in high isolated yields of 89-98 % (entries 1-7) accompanied with the elimination of the benzyl group. These yields are comparable or in some cases (entries 1 and 4) superior to those of the previous work using chlorine gas.

Other types of sulfides such as benzyl amidinium, dialkyl, and alkyl phenyl sulfides gave the corresponding sulfonyl chlorides in less satisfactory yields (entries 8, 9, and 11); especially the latter two gave mixtures of sulfonyl chlorides and sulfones. Diphenyl sulfide gave no benzenesulfonyl chloride, but only its sulfone (entry 10). These results clearly indicate that the ease of the cleavage of at least one C-S bond is important in this reaction. The four types of C-S bonds in Table 3 are cleaved in the order of amidinium C-S > benzyl C-S > alkyl C-S >> phenyl C-S, which can be attributed to the electron deficiency of the carbon α to the sulfur atom. As for the synthetic purpose, the present method is most valuable for the use of benzyl alkyl or benzyl aryl sulfides as starting materials. In addition, several other sulfur compounds such as sulfoxides and disulfides were also converted into sulfonyl chlorides in moderate to good yields (entries 13, 15 and 6).

As limitations of the reaction, a sulfide bearing a carboxyl group was unsuitable for the reaction (entry 17), similarly to the chlorination of alkenes. An acid-sensitive substrate and a thiol gave unidentified materials (entries 18 and 19).

Entry	Substrate ^a	Product	Yield (%) ^b
1	Ph~s~Ph	Ph SO ₂ Cl	98
2	Ph-S ^{Ph}	Ph-SO ₂ CI	96
3	Ph_S Ph	Ph_/SO ₂ Cl	89
4	CH3-S Ph	CH ₃ —SO ₂ CI	91 ^c
5	CH ₃ (CH ₂) ₃ —S ^A Ph	CH ₃ (CH ₂) ₃ —SO ₂ Cl	90
6	CH ₃ (CH ₂₎₅ —S ^{Ph}	CH ₃ (CH ₂) ₅ —SO ₂ Cl	93
7	CH ₃ (CH ₂) 7 -S ¹ Ph	CH ₃ (CH ₂₎₇ —SO ₂ Cl	92
8	Ph S NH ₃ Cl	Ph SO ₂ CI	65
9	CH ₃ (CH ₂) ₃ —S~(CH ₂) ₃ CH ₃	CH ₃ (CH ₂₎₃ -SO ₂ Cl	56
		CH ₃ (CH ₂) ₃ -SO ₂ -(CH ₂) ₃ CH ₃	38
10	Ph-S-Ph	Ph-SO ₂ -Ph	82
11	CH ₃ —S—Ph	Ph-SO ₂ Cl CH ₃ -SO ₂ -Ph	4 47
12	$\langle \rangle$		44
13	Ph SO Ph	Ph SO ₂ Cl	75
14	Ph SO ₂ Ph	recovered quantitatively	
15	Ph SS Ph	Ph SO ₂ CI	65 ^e
16	Ph-SS-Ph d	Ph-SO ₂ CI	56 ^e
17	CH ₃ CH ₂ O ₂ C S Ph	f	
18	l _o l_s√ol	f	
19	сн₃√у ѕн	f	

 Table 3. One-Step Synthesis of Sulfonyl Chlorides from Sulfides and Sulfur Compounds with HCI-Silica Gel and PhIO

a Substrate: 50 mg, PhIO: 4.4 eq. to the substrate, HCI-silica gel: 10 g.
b Isolated yields.
c Determined with GLC. Column: OV-1 (2 %) 1.5m. Inj. Temp.: 200°C. Column Temp.: 70°C→200°C (32°C/mit 8.8 eq. of PhIO was added.
e Yield based on the assumption of the production of 2 moles of sulfonyl chlorides from one mole of disulfides.
f Not identified.

Mechanisms of the reactions with iodosobenzene and HCl.

Estimated mechanisms of the reactions with iodosobenzene and HCl-silica gel are outlined in Schemes 2 and 3 based on the experimental results.



Scheme 2

Polymeric iodosobenzene reacts with hydrogen chloride to give an intermediate (I). In the reaction with alkenes, this intermediate (I) must attack a less hindered alkenyl carbon with the expulsion of the chloride to give an intermediate,¹⁴ which ends up with an adduct by the intermolecular or intramolecular substitution with the chloride or hydroxide, respectively. As chlorine gas-adsorbed silica gel hardly brought about the chlorination of stilbene in the absence of iodosobenzene, chlorine was not the oxidant in our reactions. In addition, when PhICl₂ was used instead of iodosobenzene, the chlorination of stilbene hardly occurred. In the chlorination of stilbene with iodosobenzene and HCl-silica gel, benzyl chloride and iodobenzene were obtained as by-products.

When tri- and tetraphenyl alkenes were used as substrates, steric hindrance of 1,1-diphenyl substituents disturbed the external attack of the chloride anion at this carbon and resulted in the production of a hydroxylated adduct or an epoxide.

As for the plausible reaction mechanisms of the synthesis of sulfonyl chlorides from sulfides, the following results suggest the reaction steps depicted in Scheme 3. As shown in Table 3, while a sulfoxide was converted to the sulfonyl chloride, a sulfone was recovered quantitatively (entries 13 and 14). This indicates that a sulfoxide must be produced as the first intermediate of the reaction steps. Further oxidation with the intermediate (I)



facilitates the substitution reaction at the benzylic carbon with a chloride anion. Although the detailed mechanistic pathways have not been established yet, this plausible mechanism is consistent with the experimental results.

The role of the pulverization in the reaction.

The role of pulverization for accelerating the reaction should be noted. In the synthesis of sulfonyl chlorides, characteristic smell of sulfonyl chlorides appeared at the early stage of pulverization. Without pulverization, a mixture of HCl-silica gel, iodosobenzene and a substrate gave only a trace amount of the products. It is thus concluded that the pulverization is an essential process to accelerate the reactions in the

	<u>.</u>		Yield (%) ^b		
Entry	Substrate ^a	Product	Solid-state	Liqliq. ^c	Liqgas ^d
1	Ph~s~Ph	Ph SO ₂ CI	98	73	54
. 2	Ph Ph		65	62	63
3	OMe OMe OMe		0 / 42 / 52	21 / 67 / 0 ^e	31 / 36 / 0 ^e
4	())		31 ^e	64 ⁰	32 ^e

 Table 4. Comparison between Yields in Solid-state Pulverization Reactions and Those in Liquid-liquid or Liquid-gas Reactions

^a Substrate: 50 mg, PhIO: 2.2eq.(entries 2 and 4) or 4.4 eq.(entries 1 and 3) to the substrate, HCI-silica gel: 10 g.

^b Isolated yields, otherwise noted.

^c Ether 50 ml/concd HCl 1 ml , vigorously stirred for 30 min.

^d During the reaction(30 min.), dried HCl gas was bubbled into the reaction mixture in ether (50 ml).

^e Determined by GLC.

absence of a solvent.

In order to establish further advantage of our solid-state reactions, several experiments were carried out, the results of which are shown in Table 4.

In Table 4, the reactivities of these reaction systems different in the phases (solid-state, liquid-liquid and liquid-gas) are compared. For the synthesis of phenylmethanesunfonyl chloride, the solid-state reaction afforded the best yield among the three. For the chlorination of stilbene, the three systems showed almost the same results. For the oxidation and chlorination of hydronaphtoquinone dimethyl ether, the solid-state reaction showed the different product selectivity from other two solution reactions. The result suggests that the side reactions with chlorine or HCl are depressed in the solid-state.

The efficiency of the encounter of the starting materials was compared in solid-solid and liquid-liquid heterogeneous systems. Figure 1 shows the yield of phenylmethanesunfonyl chloride plotted against the relative amount of iodosobenzene used. Clear difference in the relative amount of iodosobenzene showing the maximum yield is apparent. The yield of phenylmethanesunfonyl chloride obtained in the liquid-liquid reaction reached the maximum at about two equivalents of iodosobenzene, whereas that in the solid-state reaction at four. On the assumption that the reaction mechanisms are same for the two systems, the reaction efficiency of the liquid-liquid system looks higher than that of the solid-state at the smaller reagent-substrate ratio. However, it should be noted that solid-state system showed the better maximum yield. In the liquid-liquid system, a larger amount of sulfide is consumed for the side reactions with an excess HCl and/or Cl_2 to result in a lower yield of the desired product. In contrast, in the solid-state reaction the excess HCl and Cl_2 are rapidly released away from the reaction system to result in a higher reaction yield of the product.

In the present reaction system, silica gel plays a role of a solvent in a solution reaction. It makes reagent molecules to be dispersed on its surface to react efficiently. Pulverization must make the surface area larger and





- ^a Dibenzylsulfide: 50 mg / Ether 50ml/concd HCl 1 ml, vigorously stirred for 30 min.
- ^b Dibenzylsulfide: 50 mg, HCI-silica gel: 10 g.

the contact among the reagents easier. Furthermore, gradual crushing to fine particles of silica gel may cause the reaction to proceed gently. Silica gel has been known to produce silyl and sililoxy radicals¹⁵ or local hot spots¹⁶ by pulverization. Those active sites may play a role in the present reaction systems.

In conclusion, the results obtained in the present study clearly demonstrate that the pulverization of a supported reagent is the valuable activation method for organic solid-state reactions. This reaction system of multi-components should be applicable for various types of reactions

EXPERIMENTAL SECTION

Materials.

Most starting materials were commercially available (Aldrich, Nacalai Tesque, or Wako) except some sulfides which were prepared according to the known method.¹⁷ Solvents for extraction and chromatography were extra pure grade reagents and used without further purification. Identifications of all the products, which are already known, were performed according to the literature¹⁸⁻³⁸ by comparison with authentic samples. ¹H- and ¹³C-NMR and MS spectra were recorded on a JEOL GX-270 spectrometer and a Shimadzu QP-1000S mass spectrometer, respectively. Selected spectral data for some products, authentic samples of which are not commercially available, are listed below.

1,2-Dichloro-1,2-diphenyletháne (meso- or d/l mixture)¹⁸: ¹H NMR (270 MHz, CDCl₃) δ = 5.22-5.26 (s and m, 2H), 7.13-7.42 (m, 10H); ¹³C NMR (90 MHz, CDCl₃) δ = 68.73, 68.65, 129.01, 129.09, 129.13, 129.20, 138.21, 138.26; MS (EI) m/z = 250 (M⁺), 215 (M⁺-Cl), 180 (M⁺-2Cl), 125 (PhCHCl).

1,2-Dibromo-1,2-diphenylethane (meso- or d/l mixture)¹⁹: ¹H NMR (270 MHz, CDCl₃) δ = 5.48 (broad, 2H), 7.31-7.53 (m, 10H).

1,2-Dichloro-1,2-diphenylethylene²⁰: ¹H NMR (270 MHz, CDCl₃) δ = 7.26-7.63 (m, 10H); MS (EI) m/z = 250 (M*+2), 248 (M*), 212 (M*-Cl-1), 176 (M*-2Cl-2).

1,2-Dibromo-1,2-diphenylethylene²¹: ¹H NMR (270 MHz, CDCl₃) δ = 7.12-7.55 (m, 10H); MS (EI) m/z = 340 (M⁺+4), 338 (M⁺+2), 336 (M⁺), 259 (M⁺-Br+2), 257 (M⁺-Br), 178 (M⁺-2Br).

1,2-Diiodo-1,2-diphenylethylene²²: ¹H NMR (270 MHz, CDCl₃) δ = 7.42 (broad m, 10H); MS (EI) m/z = 432 (M⁺), 305 (M⁺-I), 178 (M⁺-2I).

2-Chloro-1,1-diphenylethanol²³: ¹H NMR (270 MHz, CDCl₃) δ = 3.17 (s, 1H), 4.16 (s, 2H), 7.31-7.51 (m, 10H); ¹³C NMR (90 MHz, CDCl₃) δ = 53.03, 77.70, 126.23, 127.67, 128.28, 143.11; MS (EI) m/z = 215 (M*-OH).

2-Bromo-1,1-diphenylethanol²⁴: ¹H NMR (270 MHz, CDCl₃) δ = 3.10 (s, 1H), 4.11 (s, 2H), 7.34-7.56 (m, 10H); ¹³C NMR (90 MHz, CDCl₃) δ = 43.86, 77.03, 126.18, 127.74, 128.31, 143.17; MS (EI) m/z = 261 (M*+2-OH), 259 (M*-OH).

2-Iodo-1,1-diphenylethanol²⁵: ¹H NMR (270 MHz, CDCl₃) δ = 2.87 (s, 1H), 4.00 (s, 2H), 7.36-7.46 (m, 10H); ¹³C NMR (90 MHz, CDCl₃) δ = 22.29, 77.40, 126.13, 127.73, 128.16, 143.24; MS (EI) m/z = 307 (M⁺-OH).

2-Chloro-1,1,2-triphenylethanol²⁶: ¹H NMR (270 MHz, CDCl₃) δ = 3.24 (s, 1H), 5.86 (s, 1H), 6.99-7.70 (m, 15H); ¹³C NMR (90 MHz, CDCl₃) δ = 69.00, 81.00, 126.01, 126.82, 127.15, 127. 55, 127.70, 128.02, 128.31, 129.46, 136.87, 142.43, 145.30; MS (EI) m/z = 291 (M⁺-OH).

α,α-Diphenylacetophenone²⁷: ¹H NMR (270 MHz, CDCl₃) $\delta = 6.04$ (s, 1H), 7.22-8.02 (m, 15H); ¹³C NMR selected (90 MHz, CDCl₃): $\delta = 59.20$, 199.00; MS (CI) m/z = 273 (M⁺+1); IR (KBr) v = 1685 (CO) cm⁻¹. **Tetraphenylethylene oxide**²⁸: ¹H NMR (270 MHz, CDCl₃) $\delta = 7.05$ -7.28 (m, 20H); ¹³C NMR (90 MHz, CDCl₃): $\delta = 73.7$, 127.2, 127.8, 128.2, 138.4; MS (EI) m/z = 349 (M⁺+1).

1,4-Dichloro-2,3,5,6-tetramethylbenzene¹⁹: ¹H NMR (270 MHz, CDCl₃) $\delta = 2.36$ (s, 12H); ¹³C NMR (90 MHz, CDCl₃) $\delta = 18.15$, 132.88, 133.25; MS (EI) m/z = 202 (M⁺).

1,4-Dibromo-2,3,5,6-tetramethylbenzene²⁹: ¹H NMR (270 MHz, CDCl₃) δ = 2.48 (s, 12H); ¹³C NMR (90 MHz, CDCl₃) δ = 22.3, 128.00, 134.90; MS (EI) m/z = 292 (M⁺+2).

1,4-Diiodo-2,3,5,6-tetramethylbenzene³⁰: ¹H NMR (270 MHz, CDCl₃) δ = 2.62 (s, 12H); MS (EI) m/z = 386 (M^{*}).

1-Iodo-2,3,5,6-tetramethylbenzene³⁰: ¹H NMR (270M Hz, CDCl₃) δ = 2.29 (s, 6H), 2.43 (s, 6H), 6.87 (s, 1H); MS (EI) m/z = 259 (M⁺-1).

1,2-Dichloroacenaphthene (trans/cis mixture)³¹: ¹H NMR (270 MHz, CDCl₃) δ = 5.77 (s, 2H), 7.53-7.80 (m, 6H); ¹³C NMR (90 MHz, CDCl₃) δ = 67.0, 121.9, 125.4, 129.8, 130.9, 135.0, 139.9; MS (EI) m/z = 221 (M⁺-1).

Benzyl 2-phenethyl sulfide³²: ¹H NMR (270 MHz, CDCl₃) δ = 2.59-2.65 (m, 2H), 2.77-2.83 (m, 2H), 3.66 (s, 2H), 7.09-7.28 (m, 10H); ¹³C NMR (90 MHz, CDCl₃) δ = 32.54, 35.81, 36.20, 126.08, 126.75, 128.21, 128.27,128.37, 128.42, 128.66, 138.20, 140.31.

Benzyl n-butyl sulfide³³: ¹H NMR (270 MHz, CDCl₃) $\delta = 0.87$ (t, 3H, J=8.1 Hz), 1.32-1.59 (m, 4H), 2.40 (t, 2H, J=6.8Hz), 3.70 (s, 2H), 7.19-7.30 (m, 5H); ¹³C NMR (90 MHz, CDCl₃) $\delta = 13.51$, 21.84, 30.89, 31.17, 36.17, 126.46, 128.10, 129.45, 138.53.

Benzyl n-hexyl sulfide³⁴: ¹H NMR (270 MHz, CDCl₃) $\delta = 0.87$ (t, 3H, J=6.8 Hz), 1.24-1.57 (m, 8H), 2.40 (t, 2H, J=6.8 Hz), 3.69 (s, 2H), 7.20-7.30 (m, 5H); ¹³C NMR (90 MHz, CDCl₃) $\delta = 13.86$, 22.37, 28.40, 29.04, 31.23, 31.26, 36.14, 126.67, 128.25, 128.65, 138.53.

Benzyl n-octyl sulfide³⁵: ¹H NMR (270 MHz, CDCl₃) $\delta = 0.88$ (t, 3H, J=6.8 Hz), 1.25 (m, 10H), 1.55 (m, 2H), 2.40 (t, 2H, J=8.1 Hz), 3.70 (s, 2H), 7.24-7.31 (m, 5H); ¹³C NMR (90 MHz, CDCl₃) $\delta = 13.96$, 22.52, 28.75, 29.03, 29.05, 29.10, 31.27, 31.67, 36.17, 126.70, 128.29, 128.69, 138.56.

2-Phenylethanesulfonyl chloride³⁶: ¹H NMR (270MHz, CDCl₃) δ = 3.30-3.36 (m, 2H), 3.87-3.93 (m, 2H), 7.22-7.39 (m, 5H); ¹³C NMR (90 MHz, CDCl₃) δ = 30.27, 66.01, 127.49, 128.37, 129.02, 135.43, 137.33.

Butanesulfonyl chloride³⁶: ¹H NMR (270 MHz, CDCl₃) δ = 1.00 (t, 3H, J=6.8 Hz), 1.47-1.61 (m, 2H), 1.98-2.09 (m, 2H), 3.64-3.70 (m, 2H); ¹³C NMR (90 MHz, CDCl₃) δ = 13.27, 20.78, 26.06, 65.09.

Hexanesulfonyl chloride³⁷: ¹H NMR (270 MHz, CDCl₃) $\delta = 0.91$ (t, 3H, J=6.8 Hz), 1.33-1.50 (m, 6H), 1.99-2.08 (m, 2H), 3.65-3.71 (m, 2H); ¹³C NMR (90 MHz, CDCl₃) $\delta = 13.78$, 22.21, 24.06, 27.07, 30.86, 65.21.

Octanesufonyl chloride³⁸: ¹H NMR (270 MHz, CDCl₃) $\delta = 0.89$ (t, 3H, J=6.8 Hz), 1.29-1.49 (m, 10H), 1.99-2.07 (m, 2H), 3.63-3.69 (m, 2H); ¹³C NMR (90 MHz, CDCl₃): $\delta = 13.91$, 22.43, 24.14, 27.44, 28.71, 31.49, 76.36.

General reaction procedures.

Silica gel (white, 5-10 mesh) was kept in a sealed vessel together with concd HCl solution for two weeks (HCl-silica gel) as shown in scheme 4.



Scheme 4

After this treatment, the silica gel showed an increase of its weight about 31%, which must be due to the adsorption of HCl and H_2O . HBr- and HI-silica gel were prepared similarly.

Typical reaction procedures are as follows. Iodosobenzene (270 mg, 1.23 mmol), HCl silica gel (20g), and trans-stilbene (100 mg, 0.56 mmol) were put in a mortar in this order. Be careful that some substrates such as

thiols react explosively. The mixture was crushed and ground for about 5 minutes, at the end of which the size of the silica gel was reduced to about 200 mesh. During the pulverization, rubber gloves and a face-protector should be recommended to wear, although we have not experienced any real explosion. Extraction with ether, evaporation, and column chromatography gave 90 mg of meso- and dl-1,2-dichloro-1,2-diphenylethane as major products.

Liquid-liquid and Liquid-gas reactions.

Liquid-liquid two phase reaction experiments were performed as follows. A heterogeneous mixture of a substrate (50 mg) and iodosobenzene (2.2-4.4 equivalent to the substrate) in ether (50 mL) was vigorously stirred with a magnetic stirrer. One ml of concd HCl was gradually added. After additional stirring for 30 minutes, 50 mL of ether and saturated sodium hydrogen carbonate solution were added. Extraction with ether, drying with magnesium sulfate and chromatographic purification (CH_2Cl_2 / hexane) gave the corresponding products. In the cases of liquid-gas two phase reactions, HCl gas, which was generated by the addition of concd HCl into concd H₂SO₄ and dried through a CaCl₂ tube, was bubbled into a reaction solution during the reaction. Following procedures were the same as above.

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