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Solid-State Organic Reactions Proceeding by Pulverization of Inorganic Solid-Supports. Reactions of Iodosobenzene with Unsaturated Hydrocarbons on Acid-Treated Silica Gel

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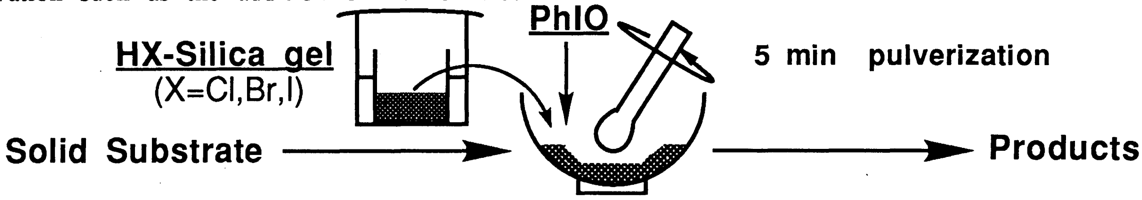
Pulverization of solid mixtures of hydrogen halide-treated silica gels, iodosobenzene, and alkenes or an alkyne in the absence of a solvent brings about smooth and rapid reaction to give halogenated or oxidized products in good yields.

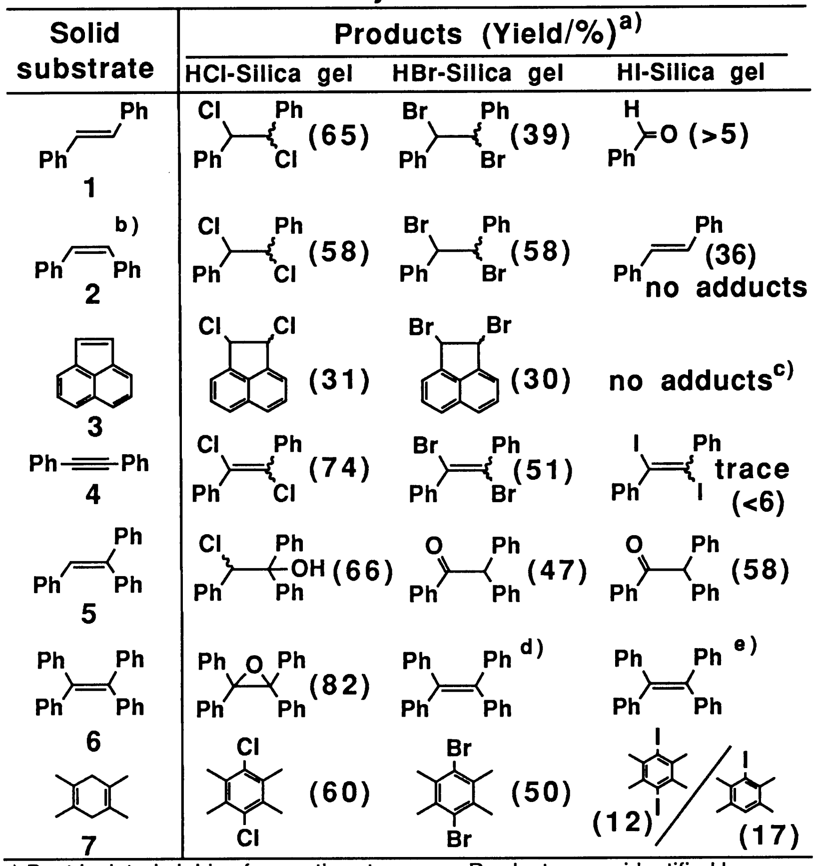
The development of solid-state organic reactions is of great interest from the mechanistic as well as synthetic point of view.[1] Recently, Toda and his group reported several examples of solid-state organic reactions which were more rapid and selective than in solution.[2] Here we present the first example of a novel type of solid-state reaction which takes place by pulverization of a mixture of solid substrates and an added inorganic solid-support in the absence of any solvent. As some inorganic solids have been known to be mechanochemically activated, we expected that pulverized silica gel surface could be used as a new reaction field for solid-state reactions. Although reported solid-state reactions usually need heat and/or time, our reactions could be completed in a few minutes by pulverization at room temperature. Moreover, we can successfully utilize the polymeric and insoluble reagent, iodosobenzene,[3] without any depolymerization-activation such as the addition of Lewis acid.



Typical reaction procedures were as follows (see above). Silica gel (Nacalai Tesque, 5-40 mesh) was kept in a sealed vessel together with concd HCl for two weeks (HCl-silica gel). HBr-silica gel and HI-silica gel were prepared similarly. A mixture of HCl-silica gel (20 g), iodosobenzene (300 mg), and *trans*-stilbene **1** (100 mg), all solid, were placed into a mortar. The mixture was crushed and ground with a pestle at room temperature for 5 minutes, at the end of which silica gel was reduced in size to about 200 mesh. Extraction with ether, evaporation, and column chromatography gave 90 mg of a mixture of *meso*- and *dl*-1,2-dichloro-1,2-diphenylethane as the major products. Noteworthy is that crushing and grinding are essential for the reaction; without these, no reaction was observed.

The reaction course and the yields of the products depended on the structure of the substrates and the kind of HX-silica gels (X=Cl,Br,I) employed (see Table 1). HCl-silica gel reacted with 1,2-

Table 1. Solid-State Reactions of Solid Alkenes and an Alkyne with Iodosobenzene



a) Best isolated yields of more than two runs. Products were identified by comparison with authentic samples or literature data. b) Oily material at r.t. c) **3** could not be recovered. d) **6** was recovered in 78% with unidentified products. e) Recovered quantitatively.

disubstituted alkenes (**1**-**3**) and an alkyne (**4**) to afford 1,2-dichlorinated 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. This observation can be attributed to the acidity of the hydrohalogenic acid; HI being too weak to activate iodosobenzene. Tri- and tetra-substituted alkenes (**5**-**7**) behaved differently from disubstituted ones and gave various interesting products as shown in Table 1. The above results indicate the intervention of $PhIX_2$ during the course of the reaction as intermediates produced from iodosobenzene and adsorbed HX, although it was not confirmed. Interesting is the fact that solid iodosobenzene can react with adsorbed HX on the surface of silica gel and then with organic solid substrates by pulverization, such as grinding in a mortar. Comparison with the reaction in solution verified that the solid-state reaction is more efficient. The reactions of **1** and **6** with iodosobenzene and concd HCl in ether gave the corresponding products in 62 and 72%, respectively. In order to evaluate the importance of adsorbed water, a dry HCl-silica gel reagent was prepared with dry HCl gas. The reaction of the reagent with **1** and **6** was essentially the same. Thus, we can conclude that the surface of the silica gel is the actual reaction field and reagent molecules on it can move dynamically as in solution.

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