

## Phase-Vanishing (PV) Reactions

Phase vanishing (PV) reactions have their origin in fluororous triphasic reactions, introduced by Curran in 2001.<sup>1</sup> In 2002, Ryu and Curran reported the first fluororous phase vanishing reaction.<sup>2</sup> The fluororous phase screen prevents the mixing of the otherwise miscible reagent and substrate phases (Figure 1). In the course of the reaction the bottom reagent phase diffuses through the fluororous phase and vanishes. The reaction occurs at the interface of the fluororous and organic phases. Thus, the fluororous phase acts as a bridging solvent that provides for the slow delivery of the reagent.

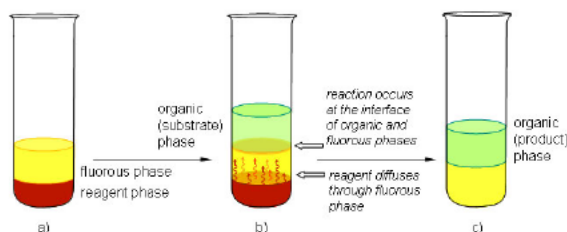


Figure 1. Conventional Phase-Vanishing (PV) Reaction.

## PV-PTFE Reactions

In a phase vanishing PTFE (PV PTFE) reaction setup, the substrate in a solvent was placed in a reaction vessel, such as a vial, a test tube or a flask (Figure 2).<sup>3-5</sup> The reagent was placed in a delivery vessel, such as a glass tube, which was sealed on both ends with PTFE tape. This tube was then inserted into the reaction vessel so that both reactants were in contact with the PTFE phase screen. In the course of the reaction the reagent diffuses through the PTFE tape into the substrate phase.

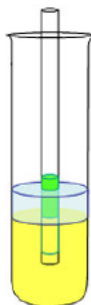


Figure 2. PV PTFE Reaction.

## Vapor Phase PV-PTFE Reactions

In a vapor phase PV PTFE reaction, substrate was placed in a flask and a PTFE sealed tube filled with a reagent was inserted into the vapor phase above it (Figure 3). When a substrate is placed in the reaction vessel, the reagent rapidly diffuses out of the tube as its vapors are consumed.<sup>4</sup> The procedure generates little or no waste while providing the reaction products in high yield and purity.



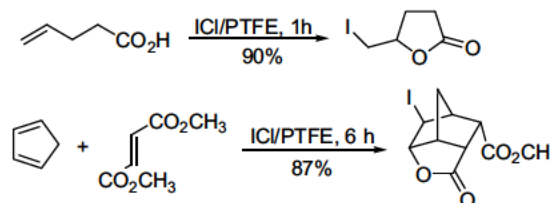
Figure 3. Vapor Phase PV PTFE Reaction.

Small vial filled with a volatile reagent, sealed with PTFE tape and inserted into a septum is a convenient way to carry out vapor phase PV PTFE reactions.



## Results

In the case of the bromination of *cis* stilbene, bromine vapors were initially rapidly consumed (Figure 3). For an *anti* addition to *cis* stilbene, it is essential that the reaction is conducted in a small flask (10 mL for 2 mmol scale reaction) and that the delivery tube is close to the surface of the substrate. Larger reaction flasks and more distant delivery tube resulted in a slower reaction and increased *syn* addition. The end of the reaction was indicated by the presence of an excess of bromine vapors. At that point, the bromine delivery tube was replaced with a reaction work up tube filled with aqueous thiosulfate. With this experimental set up, we carried reactions involving other volatile reagents such as iodine and iodine monochloride.



**Bromination of *cis* stilbene.** To a 50 mL round bottom flask a stirring bar and 0.36 mL of neat *cis* stilbene were added. A septum containing a prepared vial of bromine was inserted into the flask. The reaction was allowed to proceed until bromine vapors filled the container. A solid was recovered from the flask in approximately quantitative yield. Further purification can be accomplished by rinsing the product with a small amount of dichloromethane. The resulting *d,l* dibromostilbene has melting point of 100-110 °C.

## References

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2. I. Ryu, H. Matsubara, S. Yasuda, H. Nakamura, D. P. Curran. *J. Am. Chem. Soc.* **2002**, *124*, 12946-12947.
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