

"Surface-Mediated Reactions. 2. Addition of Hydrazoic Acid to Alkenes." Breton, G. W.; Daus, K.A.; Kropp, P.J. *Journal of Organic Chemistry* 1992, 57, 6646-6649.

Excerpt...

Organic azides are versatile intermediates for organic synthesis.<sup>2</sup> Whereas aromatic azides can be readily obtained by a variety of methods, aliphatic azides are more difficult to prepare.<sup>3</sup> Owing to its weak acidity,  $\text{HN}_3$  does not undergo electrophilic addition to alkenes except for phenyl-substituted cyclopropenes<sup>4</sup> and electron-rich alkenes, such as vinyl ethers.<sup>5,6</sup> It has been found to undergo Lewis acid catalyzed addition to styrenes and to 1,1-dialkyl and trialkyl olefins.<sup>5,7</sup> Protic acid catalyzed additions of  $\text{HN}_3$  to alkenes have also been reported,<sup>8</sup> but competing reaction of the newly formed azide with the acid catalyst frequently makes these low-yield processes.<sup>9</sup> Moreover, the necessity for generating and handling the highly toxic, and explosive,  $\text{HN}_3$  limits the convenience of both of these methods. Azide ion has been employed in conjunction with mercury(II) salts for the synthesis of secondary and tertiary azides from terminal or strained alkenes.<sup>4,10</sup> However, the method fails for simple internal alkenes such as 1-methylcyclohexene (**3**), and the disposal of mercury(II) salts is required.

Previous studies in these laboratories have shown that silica gel and alumina greatly facilitate the addition of hydrogen halides to alkenes.<sup>1</sup> Moreover, the use of appropriate precursors that generate hydrogen halides in situ on hydrolysis over silica gel or alumina makes this a particularly convenient procedure for the preparation of alkyl halides.<sup>1</sup> More recent studies have shown that the effective acidities of a number of acids are substantially enhanced on adsorption to silica gel or alumina.<sup>11</sup> We wish now to report that silica gel and alumina mediate the addition of  $\text{HN}_3$  to alkenes in the presence of an acid catalyst to give good-to-excellent yields of alkyl azides. Moreover,  $\text{HN}_3$  can be conveniently prepared in situ by hydrolysis of  $(\text{CH}_3)_3\text{SiN}_3$  over silica gel or alumina.