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Lewis Acid Promoted Annulation of *p*-Quinoneimines by Allylsilanes: A Facile Entry into Benzofused Heterocycles[†]

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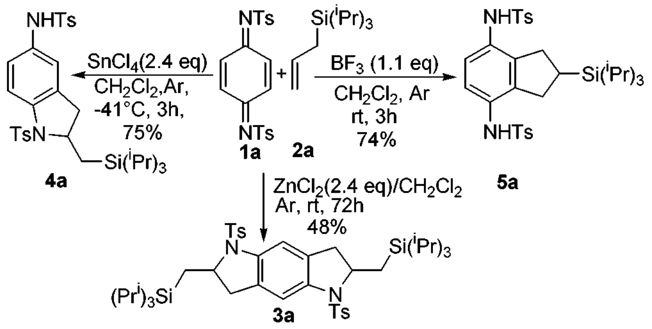
ABSTRACT



Lewis acid promoted addition of allyltriisopropylsilane to *p*-quinoneimines afforded different benzofused heterocycles in moderate to good yields depending on the conditions employed.

Benzoquinones are versatile intermediates in organic synthesis;[1] they can participate as dienes, dienophiles, heterodienes, and heterodienophiles as well as dipolarophiles in cycloaddition reactions.[2,3] In contrast to the enormous interest in the chemistry of benzoquinones, the quinoneimines,[4] their aza analogues, have received only limited attention.[5] Boger and Engler have elegantly employed the Lewis acid promoted addition of weak nucleophiles such as styrene, enamines, and allylmetals to quinoneimines to create some interesting natural product skeletons such as those of CC-1065[6] and neolignans of the type licarin-B.[7] Recently, we have reported the dipolar cycloaddition of carbonyl ylides to *p*-quinone-

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[†] This paper is dedicated with best regards and affection to Professor Gilbert Stork, whose seminal contributions have profoundly influenced organic synthesis, on the occasion of his 80th birthday.

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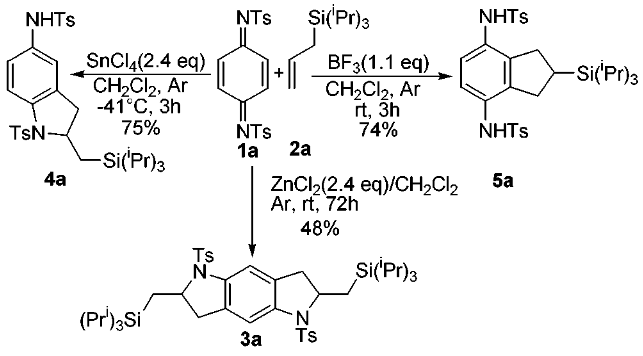
imines.[8] In this context and in view of our general interest in this area, we have undertaken an investigation of the Lewis acid promoted addition of allylsilane to quinoneimines. It is worthy of note that although a good deal of the chemistry of this silicon-stabilized nucleophile is known,[9−14] its addition to quinoneimines has remained practically unexplored. A preliminary account of some unprecedented results we have obtained are presented here.

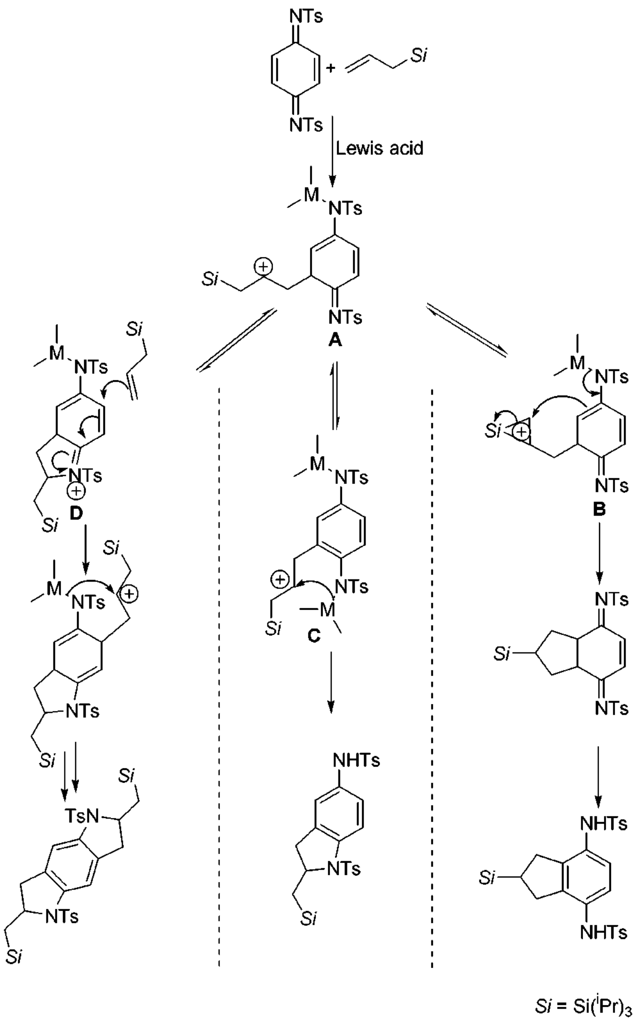
Our studies commenced by exposing a solution of *p*-quinone diimine **1a** and allylsilane **2a** in dichloromethane to $ZnCl_2$. In the event, a slow but unprecedented bisannulation of the quinoneimine by allylsilane leading to the pyrroloindole derivative **3a**, in which the two silyl groups are *trans*, occurred. The results of our optimization studies revealed a striking influence of the amount and nature of the Lewis acid used and temperature employed on the course of the reaction. For instance, when the reaction was carried out at −41 °C in the presence of 2.4 equiv of $SnCl_4$, a dihydroindole derivative arising from monoannulation resulted. Other Lewis acids also afforded the same product, albeit in lower yields (see Supporting Information). Interestingly, at room temperature, when the reaction was promoted by $BF_3{\cdot}OEt_2$ (1.1 equiv), yet another reactivity profile manifested and the product was an indane derivative (Scheme 1).[15]

Scheme 1



In the absence of any systematic study on the nature of the Lewis acid−imine complexes,[16] a plausible explanation for the formation of the above products can be furnished by invoking the chemical variants of the initially formed *β*-silylcation as shown in Scheme 2.

Scheme 2



The soft Lewis acid $ZnCl_2$ coordinates the hard tosylimine nitrogen loosely (weak hard−soft interaction). The *β*-silylcation formed initially by the addition of allylsilane to the

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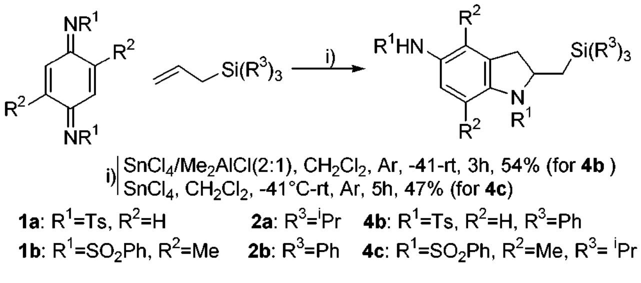
Lewis acid complexed quinoneimine is quenched by the imine nitrogen to afford an iminium species **D** as depicted in Scheme 2. This electrophilic species undergoes attack by a second molecule of allylsilane, and the quenching of the β-silylcation so formed by the enamide nitrogen affords **3a** after aromatization. An alternate explanation is that since the $ZnCl_2$-catalyzed reaction is so slow, the initially formed monoadduct is further oxidized by the unreacted iminoquinone affording an iminium intermediate that undergoes the second addition of allylsilane.[17] In the case of hard Lewis acids, $SnCl_4$ and $BF_3 \cdot OEt_2$, the initial coordination to the imine nitrogen is strong (hard−hard interaction) and hence the monocoordinated species is highly reactive. Here the stability of the β-silylcation formed holds the key. At −41 °C in the presence of $SnCl_4$, the silylcation formed is stable so that an imide−enamide-type equilibrium is established prior to the quenching of the cation. This results in the formation of **4a**. When the reaction is carried out at room temperature in the presence of $BF_3 \cdot OEt_2$, the initially formed β-silylcation is highly reactive so that the quenching of the cationic species, with a concomitant 1,2-silyl shift, through the C-terminus of the enaminoborane occurs prior to tautomerization, culminating in the formation of **5a**, which is the thermodynamically favored product. In this scheme of events, the low nucleophilicity of sulfonimide nitrogen also is important; otherwise it is likely to quench the β-silylcation as soon as it is formed (Scheme 2).

A general observation that can be made from the above study is that although lower temperature and presence of excess Lewis acid favor the formation of dihydroindole derivative, elevated temperature and stoichiometric amount of Lewis acid promote the indane derivative formation. It may be discerned that both higher temperature and excess Lewis acid would allow tautomerization to preponderate over β-silylcation quenching.[18]

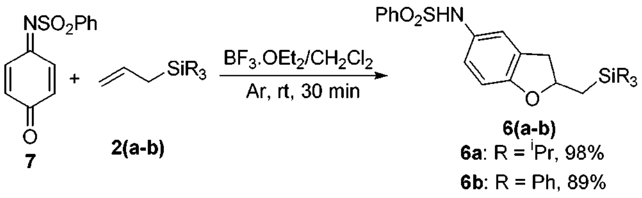
In the case of ring-substituted *p*-quinoneimine **1b**, the reaction proceeded only when promoted by $SnCl_4$, in which case the expected dihydroindole derivative resulted. When allyltriphenylsilane **2b** was employed, it required a combination of $SnCl_4/Me_2AlCl$[19] for the reaction to occur (Scheme 3).

p-Benzoquinone monoimines appeared to be impressive substrates for the present study as they offer four different electrophilic sites,[20] and their reaction seemed to be interesting both from the mechanistic and synthetic standpoints. In practice, the reaction afforded dihydrobenzofuran derivative (Scheme 4) irrespective of the Lewis acid and temperature employed (see Supporting Information). In this case, conceivably, the initial addition of allylsilane occurs in a conjugate fashion to the imine moiety. The subsequent quenching of the silylcation by the keto oxygen furnishes the dihydrobenzofuran derivative.[21]

Scheme 3



Scheme 4



Thus, from the present study it is apparent that allylsilanes undergo facile addition to *p*-quinoneimines affording formal [3 + 2] and [2 + 3] adducts. The products are substituted dihydroindole, dihydrobenzofuran, and indane derivatives. Efforts to extend the scope of the reaction and to examine further transformation of the adducts are currently underway.

Acknowledgment. C.R. and R.D. thank Council of Scientific and Industrial Research, New Delhi for research fellowships. Financial assistance from American Cyanamid Company, U.S.A. is gratefully acknowledged.

Supporting Information Available: Schemes showing effect on the reaction of the nature and amount of Lewis acid used and the temperature employed. General experimental procedure; IR, ^1H NMR and ^{13}C NMR spectral data of compounds **3a**, **4a**−**c**, **5a**, and **6a**,**b**; and single-crystal X-ray structure for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For characterization data, see Supporting Information.

(16) Denmark has spectroscopically studied the metal enolate formed by Lewis acid addition of allyltrimethylsilane to enones: Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565.

(17) The authors are thankful to a reviewer for suggesting this pathway.

(18) The ability of allylsilanes to act as either two- or three-atom components in formal dipolar cycloaddition is well precedented. It is, however, noteworthy that the versatility of the quinoneimine and the multiple reaction profiles they elicit are predicated by the availability of different nucleophilic sites and the possibility of tautomerization.

(19) It is believed that Me_2AlCl acts as a proton sponge thereby preventing the protodesilylation of the starting material, allyltriphenysilane: Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. J. *J. Am. Chem. Soc*. **1979**, *101*, 5285. For an excellent study employing Me_2AlCl in allylsilane addition, see: Organ, M. G.; Winkle, D. D.; Huffman, J. *J. Org. Chem*. **1997**, *62*, 5254.

(20) Engler, T. A.; Wanner, J. *Tetrahedron Lett*. **1997**, *38*, 6135.

(21) This contrasts with the low nucleophilicity of the imine nitrogen, which plays a crucial role in the scheme of events as mentioned earlier.