Communications to the Editor

4*H*-1,2-Benzoxazines as Novel Precursors of *o*-Benzoquinone Methide

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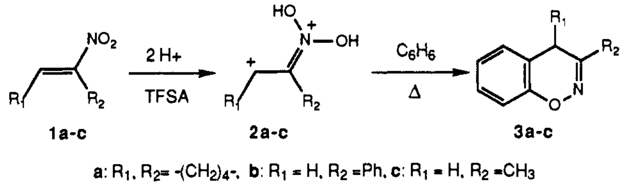
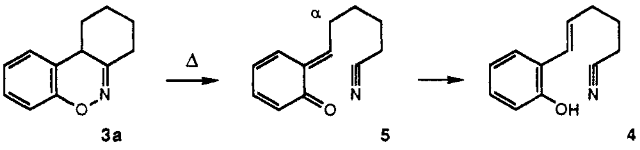
In spite of the accumulation of considerable knowledge on the formation and reactions of five-membered benzisoxazoles[1] and six-membered benzoxazines such as 1,3- and 1,4-benzoxazines,[2] no 4*H*-1,2-benzoxazine has so far been reported. We have prepared examples of this novel heterocycle, 4*H*-1,2-benzoxazine, for the first time by utilization of a novel electrophilic reagent, O,O-diprotonated nitro olefin **2**, formed in trifluoromethanesulfonic acid (TFSA): the dication formed from a nitro olefin (**1a–c**) bearing an alkyl substituent at the C_1 position reacts with benzene to give the corresponding 4*H*-1,2-benzoxazine (**3a–c**) in high yield (Scheme I).[3] In this paper we also describe a facile thermal C–N bond cleavage of 4*H*-1,2-benzoxazines to yield the corresponding *o*-benzoquinone methide, which has considerable synthetic utility.[4]

The tricyclic 4*H*-1,2-benzoxazine **3a**, formed from 1-nitrocyclohexene (**1a**), gave 2-(5-cyano-1-pentenyl)phenol (**4**) in 32% yield on heating at 190 °C (in *o*-dichlorobenzene) for 1 h (Scheme II). The formation of this product can be interpreted in terms of intervention of the *o*-benzoquinone methide **5** derived by N–O and C–C bond cleavage of **3a**.[5] Since such an *o*-benzoquinone methide is extremely reactive,[4] the involvement of *o*-benzoquinone methide in a reaction is often demonstrated by trapping with a dienophile,[6] resulting in the formation of a chroman derivative.[7] In the case of **3a**, however, we saw no evidence for Diels–Alder adduct formation in the presence of a dienophile, probably because aromatization would be rapid owing to the presence of mobile α-protons in the intermediate. Thus, we investigated the reactions of the bicyclic benzoxazines **3b** and **3c**, which were obtained by the acid-catalyzed reactions of α-nitrostyrene (**1b**) or 2-nitropropene (**1c**) with benzene, respectively.

Scheme I



Scheme II



Scheme III

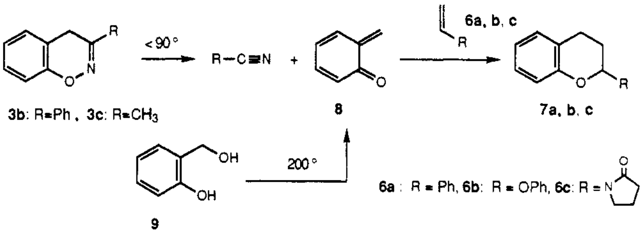


Table I. Reactions of *o*-Benzoquinone Methide with Electron-Rich Olefins

precursor	dienophile	temp., °C	time, h	yield of **7**, %
3b	**6a**	90	6.5	64
3b	**6b**	90	5.5	55
3b	**6c**	90	7	83
3c	**6a**	60	10.5	42
3c	**6b**	60	18	59
3c	**6c**	60	5	62
9	**6a**	190	2	68
9	**6b**	200	9	89
9	**6c**	200	3	49

In the presence of an electron-rich olefin **6**, such as styrene (**6a**), phenyl vinyl ether (**6b**), or *N*-vinyl-2-pyrrolidinone (**6c**), the 4*H*-1,2-benzoxazine **3b** yields the corresponding substituted chroman (**7a–c**) in a moderate to good yield by heating at 90 °C (Table I). The reaction also occurs in the case of the 4*H*-1,2-benzoxazine **3c**, resulting in the same chroman derivative as from **3b**. In the case of **3b**, the resultant benzonitrile could also be identified in all cases. In order to characterize the species formed in the reaction, thermal reactions of *o*-hydroxybenzyl alcohol **9**, a well-established precursor for *o*-benzoquinone methide **8**,[7] with the specified olefins were also carried out (Table I). Thus, the formation of the corresponding chromans from **3b** and **3c**, as well as from **9**, can be interpreted in terms of the intermediacy of *o*-benzoquinone methide **8** (Scheme III). The reaction of **9** requires a higher reaction temperature, more than 190 °C. The reactions of **3b** and **3c**, however, take place at far lower temperatures, as low as 60 °C in the latter case. These results indicate that the 4*H*-1,2-benzoxazines are novel and versatile precursors for *o*-benzoquinone methide **8**, in particular, under mild neutral conditions.

The Diels–Alder adducts, chroman derivatives **7**, obtained in all cases were found to be formed in a completely regiospecific manner (only 2-substituted chroman derivatives were produced). This can be explained in terms of the frontier orbital interaction of the LUMO of *o*-benzoquinone methide (as a diene) and the HOMO of an olefin.[7] Moreover, *o*-benzoquinone methide does not react with electron-deficient olefins such as methyl acrylate,

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(1) Lindemann, v. H.; Cissee, H. *Justus Liebigs Ann. Chem.* **1929**, *469*, 44. Blatt, A. H. *J. Am. Chem. Soc.* **1938**, *60*, 205. Reich, D. A.; Nightingale, D. V. *J. Org. Chem.* **1956**, *21*, 825. Borsche, v. W.; Herbert, A. *Justus Liebigs Ann. Chem.* **1941**, *546*, 277.

(2) (a) Fomum, Z. T.; Nkengfack, A. E.; Landor, S. R.; Landor, P. D. *J. Chem. Soc., Perkin Trans. 1*, **1988**, 277. Bowen, R. D.; Davies, D. E.; Fishwick, C. W. G.; Glasbey, T. O.; Noyce, S. J.; Storr, R. C. *Tetrahedron Lett.* **1982**, *23*, 4501. (b) Bartsch, H.; Ofne, M.; Schwarz, O.; Thomann, W. *Heterocycles* **1984**, *22*, 2789.

(3) Ohwada, T.; Ohta, T.; Shudo, K. *Tetrahedron* **1987**, *43*, 297. Ohwada, T.; Okabe, K.; Ohta, T.; Shudo, K. *Tetrahedron*, in press. The synthesized compounds **3a–c** and other new compounds have been fully characterized in terms of the NMR spectroscopy and combustion analysis (and X-ray crystallographic analysis for **3a**).

(4) Turner, A. B. *Quart. Rev.* **1964**, *18*, 347. Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* **1976**, *98*, 6040. Eck, V.; Schweing, A.; Vermeer, H. *Tetrahedron Lett.* **1978**, 2433.

(5) This reaction can also be regarded as an abnormal Beckmann rearrangement, involving N–O bond cleavage of an oxime group synchronously with a C–C bond cleavage. Conley, R.; Lange, R. *J. Org. Chem.* **1963**, *28*, 210.

(6) *o*-Benzoquinone methide, having continuous cyclic conjugation, is proposed to react as a diene rather than a dienophile. Inagaki, S.; Hirabayashi, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7418.

(7) Katada, T.; Eguchi, S.; Esahi, T.; Sasaki, T. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2649. Wagner, H.-U.; Gompper, R. *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Interscience: New York, 1975; Part 2, p 1174. Bolon, D. A. *J. Org. Chem.* **1970**, *35*, 3666.

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maleic anhydride, and acrylonitrile, whereas it does react with electron-rich olefins. That is, *o*-benzoquinone methide preferentially behaves as an *electron-deficient* diene. Therefore the reaction of *o*-benzoquinone methide with an olefin can be regarded as an example of an inverse-electron-demand Diels–Alder reaction[8] involving a neutral diene.[9]

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(8) Bradsher, C. K.; Carlson, G. L. B.; Porter, N. A.; Westerman, I. J.; Wallis, T. G. *J. Org. Chem.* **1978**, *43*, 822. Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415. Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

(9) An example of the inverse-electron-demand Diels–Alder reaction involving a cationic diene is described in the following: Gupta, R. B.; Franck, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 5393.

Catalysis by a Lewis Acid Silane for Reductions by an Analogous 10-Si-5 Hydridosiliconate[1]

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The 10-Si-5 lithium hydridosiliconate **2**, originally prepared[2] by reaction of $HSiCl_3$ with the dilithio derivative of hexafluorocumyl alcohol, is better synthesized[3] by reaction of 8-Si-4 silane **1** with $LiAlH_4$. It was found[4a,b] to be unstable when synthesized by the earlier method, probably because of the presence of destabilizing impurities. Sakurai et al.[4a] made a more stable, but not isolated, bis(phosphoranyl)iminium salt for use as a reducing agent. We also used purified tetrabutylammonium salt **4**, prepared from stable **2** as in Scheme I, and found both **2** and **4**, as well as the deuterium analogues **3** and **5**, to reduce ketones, aldehydes, etc. slowly. All were found to be much more efficient, and more selective, in the presence of silane **1** as a catalyst.

The catalyzed reduction of *p*-(dimethylamino)benzaldehyde (DMAB, **6**) in CH_2Cl_2 is kinetically third order, as shown in Scheme II. The hydridosiliconate reduction is clearly catalyzed by silane **1**. The two bidentate ligands of **1** were designed earlier,[2] with an electronegative oxygen and an electropositive carbon on each ligand, to stabilize 10-X-5 trigonal-bipyramidal hypervalent species. Silane **1** is a Lewis acid found[5] to coordinate strongly to the carbonyl oxygen of **6**. The carbonyl group becomes more electron deficient, accelerating the transfer of a hydride anion from **2** or **4** to the cationic carbon of **7** to form **8**.

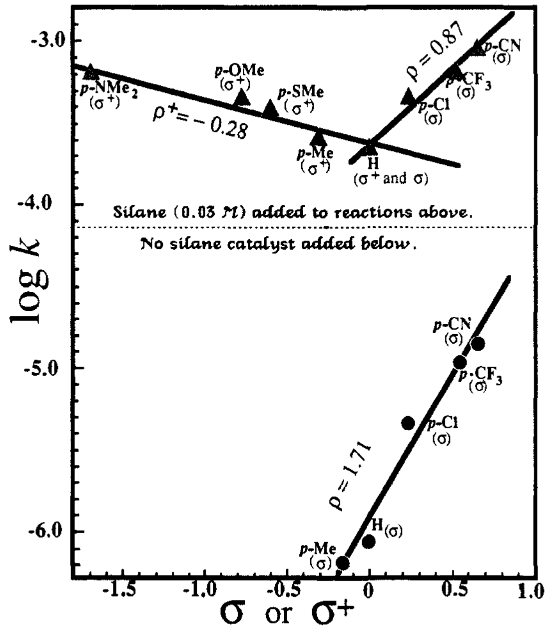
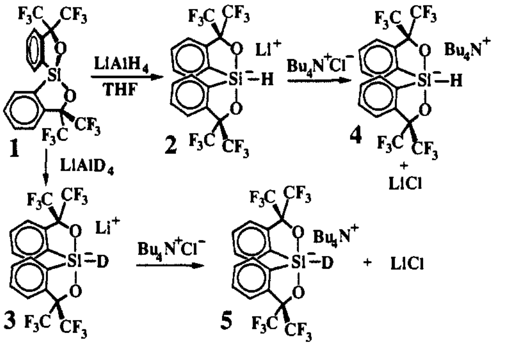
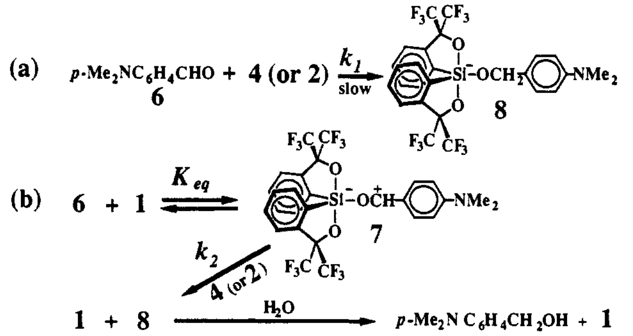


Figure 1. Log rate constants, at 24 °C, for the reduction of para-substituted benzaldehydes (0.3 M) in CH_2Cl_2 with hydridosiliconate (0.044 M), at the bottom of the graph, and in the presence of the silane (0.03 M), at the top, plotted against σ or σ^+ substituent constants.

Scheme I

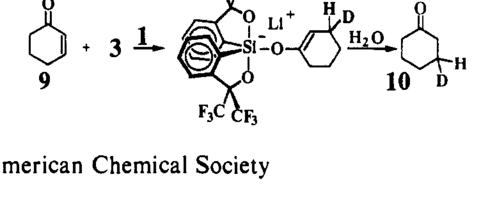


Scheme II[a]



[a] Rate = $k_1[6][4] + k_2K_{eq}[1][6][4]$.

Silane **1** catalyzes reductions of aldehydes,[6] ketones, and ketals, as well as α,β-unsaturated esters, aldehydes, ketones, and nitriles, providing 1,4-addition of the hydrides, with less 1,2-addition to the carbonyl group. For example, cyclohex-2-en-1-one (**9**) reacts with deuterated **3**, in the presence of **1**, to give only β-deuterated cyclohexanone **10**. The reduction of **9** by bis(1,2-benzenediolato)hydridosiliconate, with no silane present as a catalyst, was reported by Sakurai[7] to give only cyclohex-2-en-1-ol.



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[1] The *N*-X-*L* classification scheme characterizes species in terms of the number (*N*) of formal valence shell electrons about an atom X and the number of ligands (*L*) bonded to X. Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

[2] Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591.

[3] Silane **1** (2.44 g, 4.76 mmol) and $LiAlH_4$ (0.182 g, 4.79 mmol) in 40 mL of tetrahydrofuran were mixed at −78 °C under N_2 and warmed to room temperature over 1 h. Removal of THF followed by addition of 20 mL of ether and filtration of the AlH_3 provided **2**, which was recrystallized from ether/pentane to give 2.25 g (3.8 mmol, 80%) of **2**: mp 96–97 °C; ^{29}Si NMR δ −79.5 (d, $^1J_{Si-H}$ = 250 Hz); mass spectrum FAB *m/e* 513 (M^-). Anal. ($C_{22}H_{17}F_{12}O_3SiLi$) C, H. Solutions of **2** and Bu_4NCl in CH_2Cl_2 were mixed at −40 °C and slowly brought to room temperature. Filtration of solid LiCl was followed by recrystallization of **5**: mp 167–168 °C; ^{1}H NMR (CD_2Cl_2) δ 8.09 (dd, 2, SiCC*H*), 7.56 (d, 2, SiCCRC*H*), 7.37 (m, 4, SiCCCC*H* and SiCCHC*H*), 5.37 (s, 1, Si–*H*, with small d, $^1J_{H-Si}$ = 248 Hz), 2.99 (m, 8 NCH_2), 1.47 (m, 8, NCCH_2), 1.34 (m, 8, NCCCH_2), 0.94 (t, 12, CH_3); ^{19}F NMR (CD_2Cl_2) δ −75.33, −75.59 (2 q, 12, *J* = 8.9 Hz). Anal. ($C_{34}H_{45}F_{12}O_2SiN$) C, H, N.

[4] (a) Kira, M.; Sato, K.; Sakurai, H. *Chem. Lett.* **1987**, *46*, 2243. (b) Also determined earlier in our research.

[5] Stevenson, W. H., III; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6352.

[6] Benzaldehyde (43 mg, 0.405 mmol), hydridosiliconate **4** (303 mg, 0.416 mmol), and silane catalyst **1** (147 mg, 0.29 mmol) were dissolved in CH_2Cl_2 (1.0 mL) for 2 h at 25 °C. Solvent was removed in vacuum, and the silane was removed by washing with hexane to form solid tetrabutylammonium (benzyloxy)siliconate. Recrystallization (THF/hexane) gave 330 mg (0.383 mmol, 95%): mp 165–166.5 °C. Anal. ($C_{41}H_{51}NO_3F_{12}Si$) C, H, N. Addition of H_2O provides hydrolysis to form benzyl alcohol (completely, by ^{1}H NMR). The ^{19}F NMR spectrum of 0.7 M **4**, 0.5 M **1**, and 0.7 M in ether showed 95% formation of the (benzyloxy)siliconate within 10 min.

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