tion of fully reduced deazaFAD bound to D-amino acid oxidase.[6] Although the mechanism of the oxygen dependent reoxidation of reduced flavins is not fully understood,[8] it has been suggested that this reaction proceeds via the intermediate formation of the flavin semiquinone.[8a] Thus, the lack of oxygen reactivity of reduced deazaflavins[6] might be attributed to a slow oxidation of fully reduced deazaflavin to the deazaflavin semiquinone.

The results of this study further support the use of deazaflavins as models for elucidating the mechanism of action of flavoproteins, since it has now been demonstrated that like normal flavins, deazaflavins can exist in three chemical states, oxidized, reduced, and semiquinone. The importance of flavin semiquinones as intermediates in flavoprotein reactions is still a controversial issue.[4] The present results serve to illustrate that deazaflavin semiquinones are also potential intermediates in deazaflavoprotein catalyzed reactions.

References and Notes

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(2) (a) M. Brustlein and T. C. Bruice, *J. Am. Chem. Soc.*, **94**, 6548-6549 (1972); (b) S. Shinkai and T. C. Bruice, *ibid.*, **95**, 7526-7528 (1973); (c) D. E. Edmondson, B. Barman, and G. Tollen, *Biochemistry*, **11**, 1133-1144 (1972); (d) M. Sun and P. S. Song, *ibid.*, **12**, 4663-4669 (1973).

(3) (a) M. S. Jorns and L. B. Hersh, *J. Am. Chem. Soc.*, **96**, 4012-4013 (1974); (b) *J. Biol. Chem.*, **250**, 3620-3628 (1975); (c) J. Fisher and C. Walsh, *J. Am. Chem. Soc.*, **96**, 4345-4346 (1974); (d) B. A. Averill, A. Schonbrunn, R. H. Abeles, L. T. Weinstock, C. C. Cheng, J. Fisher, R. Spencer, and C. Walsh, *J. Biol. Chem.*, **250**, 1603-1605 (1975); (e) M. S. Jorns and L. B. Hersh, Fifth International Symposium on Flavins, and Flavoproteins, in press, (f) L. B. Hersh and M. S. Jorns, *ibid.*, in press; (g) C. Walsh, J. Fisher, R. Laura, and R. Spencer, *ibid.*, in press.

(4) T. C. Bruice, *Progr. Bioorg. Chem.*, in press.

(5) Edmondson et al.[2c] obtained evidence for the transient formation of a semiquinone form of 5-deazariboflavin by flash photolysis experiments in the presence of EDTA.

(6) L. B. Hersh and M. S. Jorns, *J. Biol. Chem.*, in press.

(7) V. Massey and G. Palmer, *Biochemistry*, **5**, 3181-3189 (1966).

(8) (a) V. Massey, G. Palmer, and D. Ballou, in *Oxidases Relat. Redox Syst.*, **1**, 25-49 (1973); (b) P. Hemmerich, A. P. Bhaduri, G. Blankenhorn, M. Brustlein, W. Haas, and W. R. Knappe, *ibid.*, **1**, 3-24 (1973).

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(10) Recipient of a Research Career Development Award GM30962.

Louis B. Hersh,*[9] Marilyn Schuman Jorns
Julian Peterson,[10] Mark Currie
Department of Biochemistry, The University of Texas
Health Science Center at Dallas
Dallas, Texas 75235

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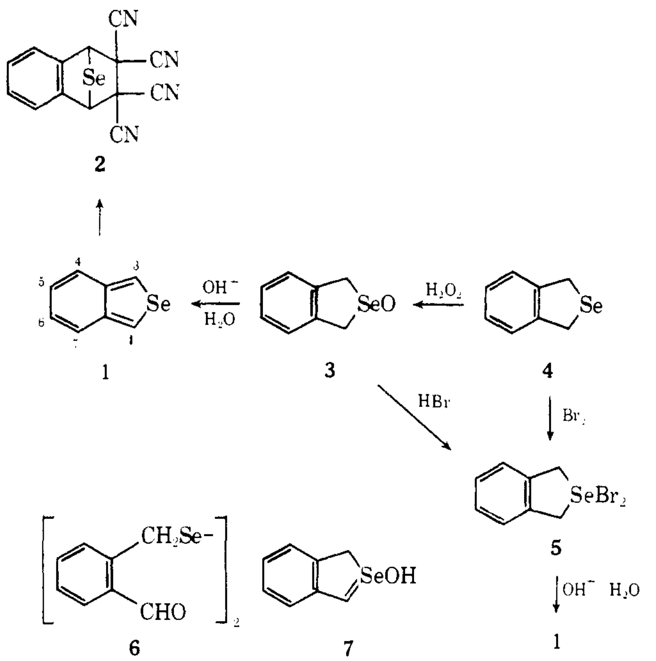
Benzo[c]selenophene. A Base-Catalyzed Selenoxide Dehydration

Sir:

The highly reactive *o*-quinonoid heterocycles benzo[*c*]furan[1] and benzo[*c*]thiophene[2] have been the objects of considerable chemical interest, both from the synthetic and the theoretical points of view. The selenium analogue of these compounds, benzo[*c*]selenophene (**1**), has hitherto remained unknown, even in the form of substitution products. We now describe the first synthesis of the unstable benzo[*c*]selenophene (**1**), as well as the first instance of a base-catalyzed dehydration of a selenoxide.

Dibenzyl selenoxide (**9**) is readily prepared in high yield either by the hydrogen peroxide oxidation of dibenzyl selenide (**8**)[3] or by treatment of dibromide **10** with aqueous alkali.[4] By contrast, oxidation of 2-selenaindane (**4**) has yielded only an anomalous product[5] now recognized as 2,2′-diformyldibenzyl diselenide (**6**),[6] whereas treatment of the corresponding dibromide **5** with alkali was stated to effect debromination to the original selenide **4**.[5] Since the reductive debromination of a selenide dibromide by base has no precedent, we reexamined this reaction with the following results.



$(C_6H_5CH_2)_2Se$ **8** $(C_6H_5CH_2)_2SeO$ **9** $(C_6H_5CH_2)_2SeBr_2$ **10**

Dibromide **5** was destroyed within a few minutes when rubbed with cold aqueous 15% NaOH. When the resulting milky emulsion was stirred at 0 °C with hexane, benzo[*c*]selenophene (**1**) was slowly liberated and extracted into the organic phase. Heterocycle **1**, which has a pronounced naphthalene-like odor, polymerized upon attempted isolation in the pure state but was found to be fairly stable as a dilute hexane solution. Its ultraviolet absorption spectrum is very similar to that of benzo[*c*]thiophene,[7] compared to which it shows a small (ca. 7 nm) bathochromic shift: λ_{max} (hexane) 273, 286, 291, 298, 302 sh, 305 sh, 312, 323, 328, 336 sh, 340, 344 sh, 353, 357, 362 sh nm. The rate of formation of **1**, as monitored by uv, increases with alkali concentration, and the reaction is best carried out using cold 40% NaOH for 2 h.

Benzo[*c*]selenophene (**1**) reacts rapidly with tetracyanoethylene in benzene (32% based on dibromide **5**) to give the highly crystalline adduct **2**, mp 220 °C dec.[8] The mass spectrum of this adduct is in full accord with the assigned structure, showing major peaks at *m/e* 310 (M, 8%), 230 (M − Se, 7%), 128 (TCNE, 66%), 182 (M − TCNE, 99%), and 102 (M − TCNE − Se, 100%).

The NMR spectrum of **1** in $CDCl_3$ showed the following peaks: δ 8.40 (s, 2 H, H_1 and H_3), 7.33-7.54 (m, AA′ part of AA′BB′, 2 H, H_4 and H_7), and 6.77-7.02 (m, BB′ part of AA′BB′, 2 H, H_5 and H_6).[9] These peaks vanished immediately upon addition of TCNE, and adduct **2** crystallized from the solution.

Since the generation of selenophene **1** from dibromide **5** can be rationalized without requiring the intermediacy of selenoxide **3**, we examined the oxidation of selenide **4** with 1 equiv of neutral H_2O_2 in cold methanol. Immediate dilution of the reaction mixture with water and CCl_4 extraction yielded only traces of starting material from the organic phase. The aqueous phase contained selenoxide **3**, since addition of HBr caused the immediate precipitation of dibromide **5** (50% pure material after ether washing). A similarly prepared neutral solution of selenoxide **3** liberated selenophene **1** very slowly into hexane until 40% NaOH was added, when rapid liberation of **1** occurred. Dehydration of the selenoxide hydrate, via the ylide **7**, would appear to be a likely mechanism for this unprecedented reaction.

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References and Notes

(1) (a) D. Wege, *Tetrahedron Lett.*, 2337 (1971); (b) R. N. Warrener, *J. Am. Chem. Soc.*, **93**, 2346 (1971).

(2) For a general review of benzo[*c*]thiophenes, see B. Iddon, *Adv. Heterocycl. Chem.* **14**, 331 (1972).

(3) H. Rheinboldt and E. Giesbrecht, *J. Am. Chem. Soc.*, **69**, 644 (1947).

(4) W. Strecker and A. Willing, *Ber.*, **48**, 204 (1915).

(5) N. N. Magdesieva and V. A. Vdouin, *Khim. Geterotsikl. Soedin.*, **8**, 24 (1972).

(6) B. E. Norcross and R. L. Martin, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975, Abstract ORGN-93.

(7) R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, **20**, 244 (1963).

(8) Adduct **2** gave satisfactory elemental analyses; it was also characterized by its NMR spectrum (DMSO-d_6): δ 6.03 (s, 2 H), 7.18–7.63 (m, 4 H). The analogous adduct of TCNE and isothianaphthene showed δ 6.2 0 (s, 2 H), 7.20–7.70 (m, 4 H).

(9) By comparison, the values ($CDCl_3$) for H_1 and H_3 for isothianaphthene (previously unreported) and isobenzofuran[1a] are δ 7.63 and 8.00. The same relative positions (δ 7.70, 7.19, and 7.40) have been observed for the α-protons of selenophene, thiophene, and furan, respectively: L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, New York, 1969, p 209.

Lydia E. Saris, Michael P. Cava*

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19174

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Evidence for the Dimerization of Dimethylsilylene to Tetramethyldisilene

Sir:

In studying the mechanisms of silylene reactions we have uncovered evidence for the gas-phase dimerization of dimethylsilylene to tetramethyldisilene.

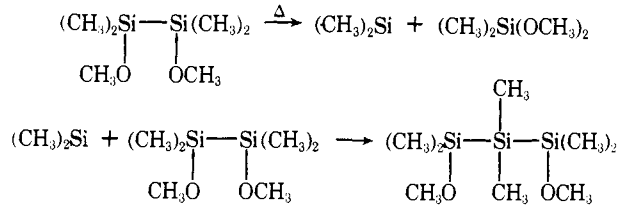
$$2(CH_3)_2Si \rightarrow (CH_3)_2Si{=}Si(CH_3)_2$$

Since these observations point to a new reaction of silylene and to a new route to sila-olefins, they seem worth reporting.

The pyrolysis of disilane and its derivatives is a well-established method for the generation of divalent silicon species, silylenes.[1]

$$RR'R''Si{-}SiRR'R'' \xrightarrow{\Delta} RR'Si + SiRR'R''_2$$

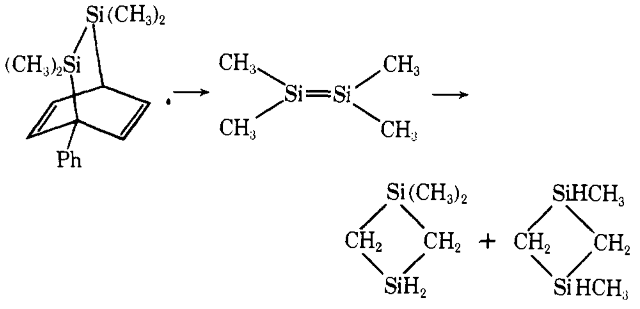
When 1,2-dimethoxy-1,1,2,2-tetramethyldisilane is subjected to gas-phase pyrolysis at low pressure (<100 μ) in a flow system at 600 °C, dissociation to dimethylsilylene is indicated by a quantitative yield of dimethoxydimethylsilane and a 14% yield of the product of attack of dimethylsilylene on its parent disilane,[2] 1,3-dimethoxy-1,1,2,2,3,3-hexamethyltrisilane.



$$(CH_3)_2Si(OCH_3){-}Si(CH_3)_2(OCH_3) \xrightarrow{\Delta} (CH_3)_2Si + (CH_3)_2Si(OCH_3)_2$$

$$(CH_3)_2Si + (CH_3)_2Si(OCH_3){-}Si(CH_3)_2(OCH_3) \rightarrow (CH_3)_2Si(OCH_3){-}Si(CH_3)_2{-}Si(CH_3)_2(OCH_3)$$

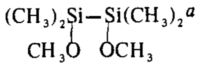
In addition, however, three disilacyclobutanes are obtained in combined yield of 28%, the two formed in greatest yield having previously been characterized as the major stable products resulting from the rearrangement of tetramethyldisilene.[3]

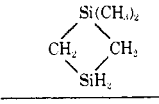
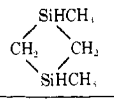
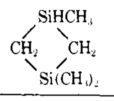
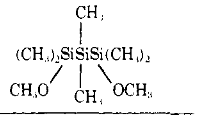


1 2

The formation of the same major products from pyrolysis of dimethoxytetramethyldisilane and from tetramethyldisilabicyclooctadienes suggests that tetramethyldisilene may be a common intermediate in the two systems and is formed by dimerization of dimethylsilylene in the former case.

In this communication we wish to summarize briefly our evidence for the formation of disilacyclobutane products, present data consistent with the formation of these products

Table I. Product Yields from Pyrolysis of  $(CH_3)_2Si(OCH_3){-}Si(CH_3)_2(OCH_3)$[a]

Temp, °C	% dec of disilane	Product yield, %[b]				
		$(CH_3)_3SiH$				
		(A. No added substrate)				
600	40	None detected	12	14	2	14
700	94	4	10	17	8	2
700	92	4	8	13	6	1
		(B. Tenfold excess of $CH_3C{\equiv}CH$[c])				$(CH_3)_3SiHC{\equiv}CCH_3$
620	49	None detected	<1	<1	<1	43
740	100	2	5	9	4	25

[a] All pyrolyses employed a seasoned hot zone consisting of a 10 mm i.d. × 12 cm quartz tube. The temperatures are measured at the outer surface of the tube. Products are condensed at 77 K within 2 cm of the hot zone. The disilane vapor flowed into the hot zone at a rate of ca. 200 mg/h, and a total of 200 or 400 mg was pyrolyzed in each experiment. [b] All yields were determined relative to the $(CH_3)_2Si(OCH_3)_2$ product. [c] When propyne was present no trisilane product was detected.