warmup. In a glass doped with Et_3SiH, warmup yielded the expected trapping product.[11]

We conclude that both **8** and **9** are photochemical precursors for the yellow species originally assigned as **6**.

The evidence for the assignment is as follows: (i) The formation of this molecule (as characterzed by its broad visible band with λ_{max} = 450 nm and its rich IR spectrum) has now been directly observed using seven widely different precursors (**1–5**, **8**, and **9**) which only possess the SiC_2H_6 moiety in common (for **2** and **9**, only the visible spectra were measured). In each case, the formation of **6** was precedented or at least plausible.[12] Since **2**, **3**, and **8** only contain one Si atom, so does the yellow species. The reversible photochemical interconversion[3–6] of the yellow species with **3** in matrix isolation proves that the two molecules are isomeric; note that the independent access to **3** by pyrolysis of **10** is secured beyond reasonable doubt.[6]

(ii) Chemical trapping experiments with Et_3SiH,[3] $Me_3SiC{\equiv}CSiMe_3$,[3] $n\text{-}C_4H_9CH{=}CH_2$,[3] N_2O,[13] and oxirane[13] yield the expected trapping products; their formation in N_2O and oxirane-doped matrices was directly followed by spectroscopy.

(iii) The 450-nm transition has the expected energy,[14] polarization,[5] band shape, and fluorescence Stokes shift.[3] The pattern of IR frequencies is very similar to those of $SnMe_2$[16] and $GeMe_2$,[17] fits qualitative expectations, and agrees with MNDO calculations.[5] Both IR bands for which a comparison is presently possible have the correct polarizations.

(iv) The species yields no ESR signal and is stable indefinitely in matrix isolation, as expected for the ground state of a simple silylene.

Before the proposed reassignment[7,8] could be seriously considered, an alternative interpretation of (i)–(iv) would have to be found. None has been suggested,[7,8] nor have we been able to think of any. The conclusion that the yellow species is ground-state dimethylsilylene **6** seems inescapable.

It is conceivable that the 350-nm species observed in the flash photolysis experiments[8] also is ground-state **6** as suggested[8] and that the 100-nm shift is due to the difference in the temperature and/or viscosity of the hydrocarbon environment. This explanation seems unlikely since spectra of the yellow species taken at 10 and 77 K do not differ much and a wide variation in the nature of the matrix has a clearly detectable but much smaller effect. Why, then, was **6** most likely not observed in the flash photolysis experiments, and what is the 350-nm species?

It is perhaps appropriate to indicate a few possibilities that have not been considered in print.[7,8] Most likely, ground-state **6** has escaped detection because its 450-nm absorption band is relatively weak and very broad (10^{-4} M solutions were used[8]). It is also conceivable that it is formed on a time-scale slower than 8 μs, either from the 350-nm species or from an unobserved species, and that dimerization then interferes with a buildup of its concentration. The 350-nm species could be, for instance, a minor ground-state or triplet-state byproduct with a high extinction coefficient which happens to be quenched with Et_3SiH and MeOH, or it could be a ground-state or excited-state intermediate in the production of ground-state **6**, such as the lowest triplet state of **6**.[18] The notion that the 350-nm absorption is due to an electronically excited species is in line with its solvent-independent unimolecular decay with a 8-μs lifetime, a property for which no interpretation has been proposed[8] and which is not expected of ground-state **6** in inert solvents. In the absence of adventitious scavenger impurities, **6** should decay in a second-order process and, at the low precursor concentrations used, more slowly, even if its dimerization is diffusion controlled. In summary, we believe that alternative interpretations of the presently available flash photolytic data exist.

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Registry No. 6, 6376-86-9; **8**, 4774-73-6; **9**, 4098-97-9; $PhMe_2SiLi$, 3839-31-4; Me_2SiCl_2, 75-78-5; Et_3SiH, 617-86-7; $Me_2PhSiSiPhMe_2$, 1145-98-8; $Et_3SiSiMe_2H$, 31732-54-4.

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(11) Irradiation for 6 h led to 74% conversion. GLC analysis after warmup revealed the presence of $Me_2PhSi\text{-}SiPhMe_2$(29%) and $Et_3SiSiMe_2H$ (43%).

(12) Matrix photolysis of geminal diazides in the carbon series leads to carbenes: Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931. The behavior in solution is different: Moriarty, R. M.; Kleigman, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 5959. Solution irradiation of geminal diazidosilanes did not produce evidence for silylenes: Ando, W.; Tsumaki, H.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1981**, 597.

(13) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176.

(14) The absorption spectrum of SiH_2 is established beyond doubt and extends from 480 to 650 nm; Buerger, H.; Eujen, R. *Top. Curr. Chem.* **1974**, *50*, 19. Numerous polysilane precursors of substituted organic silylenes other than **6** have been irradiated in rigid glasses, yielding products with broad visible absorption bands similar to that of **6**, with λ_{max} (77 K, 3MP) ranging from 400 to 580 nm (the values for a series of alkylsilylenes correlate with excitation energies calculated by the INDO/S method). They have been identified as substituted silylenes by trapping reactions (unpublished results: cf. ref 15). Methylsilylene [λ_{max} (77 K, 3MP) = 480 nm], when prepared by rearrangement of silaethylene,[6] has λ_{max} (10 K, Ar) = 480 nm. In the case of phenylmethylsilylene [λ_{max} (77 K, 3MP) = 490 nm] a room-temperature flash photolysis of a 10^{-3} M trisilane precursor yielded a transient with λ_{max} (room temperature, C_6H_{12}) = 440 nm which decayed within tens of μs with second-order kinetis and showed high reactivity toward O_2, and unexpectedly low reactivity toward several other trapping agents. The transient was tentatively assigned as PhSiMe. The shift in λ_{max} might be due to conformational effects, since rotation about the Ph–Si bond may well be nearly free, but it is also possible that the transient is not ground-state PhSiMe: Gaspar, P. P.; Boo, B. H.; Chari, S.; Ghosh, A. K.; Holten, D.; Kirmaier, C.; Konieczny, S. *Chem. Phys. Lett.* **1984**, *105*, 153.

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Selective Alkali Metal and Hydrogen Reduction of Benzene to Cyclohexene

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In connection with our interest of developing catalytic systems for the selective hydrogenation of arenes to cyclic olefins,[2] we have explored the reactivity of benzene and other aromatic radical anion systems with molecular hydrogen. Deep blue solutions containing the benzene radical anion are typically prepared at subambient temperatures by contacting benzene with alkali metals in the presence of ether solvents[3] or of cation-complexing crown ethers and cryptands.[4] In our experience, benzene solutions of the cryptand C222 ether[5] in the presence of Na/K alloy rapidly

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Table I. Benzene Reductions with Na/K and H_2

amine (mmol)	C_6H_6, mmol	Na/K, mg	H_2, atm	time, h	conv C_6H_6, %	sel C_6H_{10},[a] %
HMHCY (0.68)	5.9	1500	10.2	19	45	99.8[b]
HMHCY (0.69)	10.2	Na (212), K (16)	10.2	40	17	99.9[b]
iso-HMTT (0.94)	11.4	171	9.5	21	5	100.0[d,e]
iso-HMTT (1.3)	11.4	1500	68[c]	20	11	96.2[d,e]
HMTT (1.1)	8.0	131	8.2	40	9.9	100.0[d]
OMPEH (0.96)	10.9	206	9.5	16	1.5	100.0[d,e]

[a] Selectivity (%) = 100 $[C_6H_{10}]/([C_6H_{10}] + [C_6H_{12}])$. [b] With extensive degradation of amine. [c] Stainless steel reactor. [d] Chromatogram showed no evidence of amine degradation. [e] Traces of phenyl cyclohexane also formed.

degrade at room temperature, and we thus sought to find more chemically resistant cation-complexing agents.

We observed that upon contacting the tertiary crown amine hexamethylhexacyclen[6] [(HMHCY) $-[CH_2CH_2N(CH_3)-]_6$] as a neat liquid, with Na/K alloy (78 w/w % K) at ~20 °C, a light blue coloration develops, which darkens considerably upon the addition of benzene. The deep blue color persists for ca. 30 min at room temperature. EPR spectra of the solutions (at ca. 5 °C) display the seven-line multiplet at $g = 2.004$, with $a_H = 3.4$ G, characteristic of the benzene radical anion.[3,4] Reaction of stirred solutions of benzene and HMHCY, with Na/K and hydrogen (10 atm) at ca. 20 °C, in a heavy-wall glass tube resulted in the reduction of benzene to cyclohexene, accompanied by the formation of a white precipitate of alkali metal hydride. At a 45% conversion of benzene, cyclohexene was formed at a remarkable 99.8% selectivity with respect to cyclohexane (see Table I). We view the overall reaction taking place[7] as

$$C_6H_6 + 4M + 4H_2 \xrightarrow{\text{HMHCY}} C_6H_{10} + 4MH \qquad (1)$$

In a control experiment with no added hydrogen, small amounts of cyclohexane were seen as the only identifiable benzene reduction product.

Reaction 1 is analogous to the familiar Birch reduction[8] of aromatics except that in this case the proton source is molecular hydrogen. The observed high selectivity to cyclohexene is presumably due to its lower electron affinity than benzene and cyclic dienes.[9] Interestingly, the reaction did not take place when sodium dispersion was used instead of Na/K alloy. However, addition of catalytic amounts of potassium metal[10] resulted in the formation of cyclohexene and a solid byproduct, identified by powder X-ray diffraction as largely sodium hydride.

These appear to be the first observations of the discrete reduction of an arene using alkali metals and molecular hydrogen. Tamaru et al.[11] have extensively studied the reactivity of solid-state sodium–aromatic polynuclear hydrocarbon, electron donor–acceptor complexes with hydrogen and have spectroscopically detected monohydro aromatic reduction products. However, in other work, the reaction of sodium naphthalene in tetrahydrofuran with H_2 at 40 °C was shown to yield only naphthalene and sodium hydride.[12]

Since the metal hydride byproduct of reaction 1 could in principle be thermally dissociated to recover metal and hydrogen,[13] the transformation might be viewed as permitting an overall, selective hydrogen reduction of benzene to cyclohexene. Unfortunately, the reaction was always accompanied by an extensive degradation of the HMHCY amine. Attempts to overcome this difficulty by the use of the analogous tetraaza and pentaaza cyclic amines were unsuccessful. We then examined linear and branched tertiary *N*-methyl polyamines as possible cation complexing agents and discovered, surprisingly, that these amines could also promote the reduction of aromatics.

Benzene solutions of tris[[2-(dimethylamino)ethyl]amine] [$N[CH_2CH_2N(CH_3)_2]_3$ (iso-HMTT)][14] in contact with Na/K gave an initial yellow color and a weak unresolved EPR resonance. After several days of stirring at room temperature, the characteristic septet at $g = 2.005$; $\langle a \rangle = 3.5$ G, of the benzene radical anion was seen. After further aging (>7 days), the EPR spectrum showed a multiplet at $g = 2.005$, $\langle a \rangle = 5.4, 2.7, 0.44$ G, characteristic of the biphenyl radical anion.[15,3c] Reaction of benzene, iso-HMTT, Na/K, and hydrogen over 40 h resulted in a 5% conversion of benzene to cyclohexene in 100.0% selectivity with respect to cyclohexane (Table I). Traces of phenylcyclohexane presumably formed by a reduction of the biphenyl radical anion were also seen. The iso-HMTT catalyst appears to be unaffected; careful analysis by gas chromatography showed no evidence of amine degradation products. Improved conversion to cyclohexene was realized at higher H_2 pressures but with attendant loss in selectivity, which is possibly attributable to some hydrogenation of cyclohexene catalyzed by the steel reactor walls. The highly branched potentially chelating amine octamethylpentaethylenehexamine[16] [(OMPEH) $[(CH_3)_2NCH_2CH_2]_2NCH_2CH_2N[CH_2CH_2N(CH_3)_2]_2$] was surprisingly much less effective than *n*-hexamethyltriethylenetetramine[14] [(HMTT) $(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$]. A multiple nitrogen coordination of the alkali metal cation seems to be important since *N,N,N′,N′*-tetramethylethylenediamine did not promote the Na/K, benzene/H_2 reaction.

Limited studies were done using other arenes. Toluene (9.2 mmol) and H_2 (9.5 atm) reacted with excess Na/K, in the presence of iso-HMTT (1.3 mmol), in 16 h, with 4% conversion to a 1:0.92 mixture of 1-methyl-1-cyclohexene and 1-methyl-3-cyclohexene. Under similar conditions, reduction of biphenyl gave only phenylcyclohexane. Reduction of naphthalene, using Na dispersion instead of Na/K, gave 1,2,3,4-tetrahydronaphthalene. This is in contrast to previous work, cited earlier, where in tetrahydrofuran no hydrogenated naphthalenes were formed.[12] Blue solutions prepared from sodium, 12-crown-4 ether, and benzene, which reportedly contain the benzene radical anion,[4d] afforded only traces (<0.01% conversion) of cyclohexene and cyclohexane upon contact with hydrogen (7.9 atm, 18 h). The surprising reactivity of aromatic negative ion species in tertiary polyamines with hydrogen might be attributed to a lower stabilization of the

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(5) Formally: 4,7,13,16,21,24-hexaoxyl-1,10-diazabicyclo[8.8.8]hexacosane.

(6) Formally: 1,4,7,10,13,16-hexaza-1,4,7,10,13,16-hexamethylcyclooctadecane. Barrett, A. G. M.; Godfrey, C. R. A.; Hollinshead, D. M.; Prokopiou, P. A.; Barton, D. H. R.; Boar, R. B.; Joukhar, L.; McGhie, J. F.; Misra, S. C. *J. Chem. Soc., Perkin Trans 1* **1981**, 1501.

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cation–arene anion ion pair species than in traditional ether solvents.

Registry No. HMHCY, 79676-97-4; *i*-HMTT, 33527-91-2; HMTT, 3083-10-1; OMPEH, 96412-47-4; C_6H_6, 71-43-2; *c*-C_6H_{11}Ph, 827-52-1; MePh, 108-88-3; Ph_2, 92-52-4; cyclohexene, 110-83-8; 1-methyl-1-cyclohexene, 591-49-1; 1-methyl-3-cyclohexene, 591-47-9; naphthalene, 91-20-3; 1,2,3,4-tetrahydronaphthalene, 119-64-2; cyclohexane, 110-82-7.

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o-Hydroperoxynaphthoquinols. Chemical Transducers for Coupling Oxidation with Acylation: A Vitamin K Model

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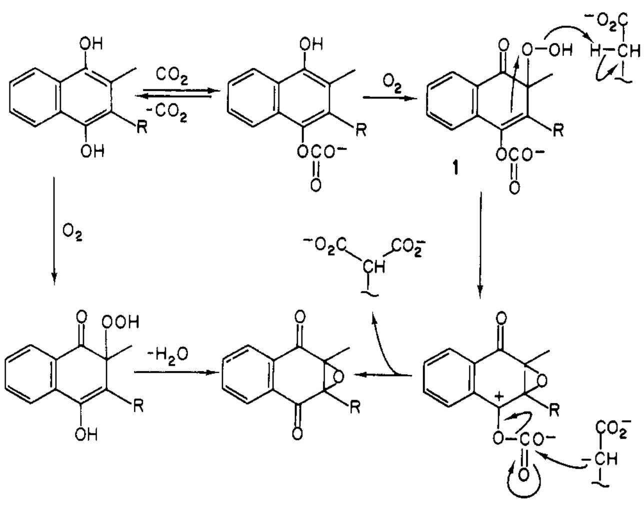
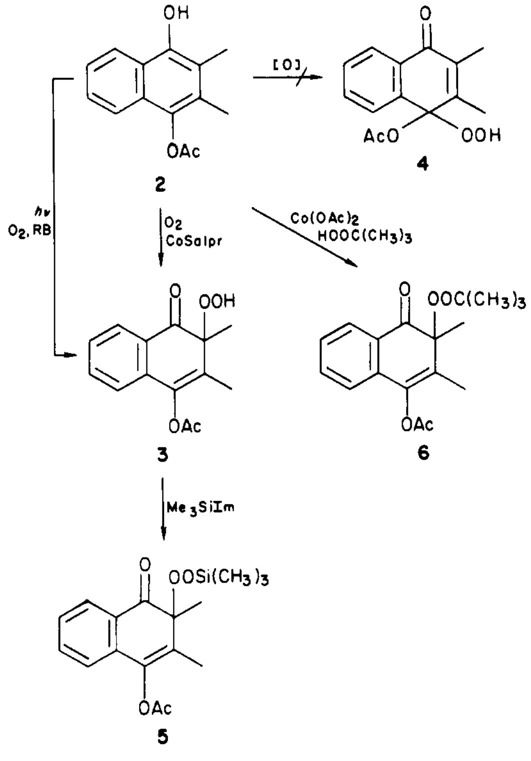
Vitamin K is an essential cofactor for a number of important biological processes[1,2] and yet only on the coagulation of blood[3] has a well-defined chemical role for vitamin K been proposed. Suttie has suggested that hydroperoxides of vitamin K[4] are involved in the carboxylation of glutamic acid residues of blood proteins.[5] While the mechanism of this carboxylation is still uncertain, the working hypothesis outlined in Scheme I is consistent with the available data.[4,5a] Our interest in the chemistry of vitamin K peroxides[6] has prompted us to synthesize peroxides related to **1** and to study their chemistry in an effort to evaluate Suttie's proposal.

A number of synthetic approaches to hydroperoxides related to **1** have been examined (Scheme II). These approaches all begin with the hydronaphthoquinone monoacetate **2** which is readily available through partial hydrolysis of the corresponding diacetate.[7] In the initial approach, photochemically generated singlet oxygen was employed as the oxidizing agent. While the hydroperoxide **3** was formed under these conditions, the yields were very poor (~10%). Subsequently it was found that **3** could be obtained in quantities useful for further study (34%) using cobalt salpr and molecular oxygen.[8] The success of this method is most intriguing since oxygen-binding cobalt complexes of this type are considered to be good models for the iron-containing cytochrome oxidizing agents of biological systems.[9]

Scheme I



Scheme II



That this hydroperoxide[10] (mp 154.1–156.0 °C) was indeed the ortho hydroperoxide isomer **3** and not the para hydroperoxide isomer **4** is most apparent from the IR spectrum which has ν_{max} at 1760 and 1670 cm^{-1} for the enol acetate and 1695 cm^{-1} for the aryl ketone. In addition, the UV spectrum, $\lambda_{max}(CH_3CN)$ 235 nm (ϵ 24600), 270 (1640), 277 (1730), 287 (1130), and 337 (870), was consistent with **3** but quite different from that of a model containing the cross-conjugated carbonyl chromophore in **4**.[11]

Peroxide derivatives of **3** are also readily available (Scheme II). (Trimethylsilyl)imidazole smoothly converts **3** to **5** (65%, mp 95.8–97.4 °C). The *tert*-butyl peroxide **6** is particularly easy to

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