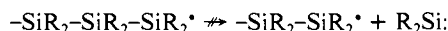
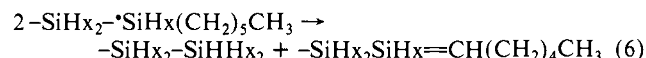
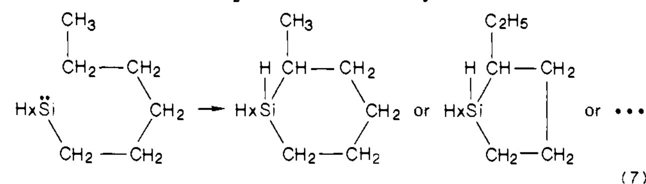
has also recently been shown for $Me_3SiSiMe_2^\bullet$.[13] Above 300 nm, products such as $H(SiR_2)_nH$ (n = 2, 3) are not formed either, since Si_nR_{n+2} is transparent for $n < \sim 7$.[14]



Irradiation (308 nm) of p-(Hx_2Si) or p-(Hx_2Si-β-D), fully β-deuterated on the n-hexyl side chains in pentane, pentane-d_{12}, cyclohexane, cyclohexane-d_{12}, or Et_3SiD, produces only Si–H and no Si–D bonds (IR); p-(Hx_2Si-α-D), fully α-deuterated on the hexyls, forms Si–D and no Si–H bonds. We conclude (iv) that in addition to likely recombination, the primary radicals undergo disproportionation[2,7,9] but not a more or less random hydrogen abstraction from solvent[2] or polymer side-chains to yield carbon radicals.[4] Similarly there is no evidence of intermolecular radical abstraction from Et_3SiD when incorporated in the solvent.



Repetition of steps 2 and 6 accounts for the observed formation of $H(SiHx_2)_nH$ (n = 2, 3). We have no information on the subsequent fate of the silene formed in (6) such as dimerization or addition of $-SiHx_2-{}^\bullet SiHx_2$ followed by further transformations. The formation of Si–H in addition to Si–D bonds upon 248-nm irradiation of p-(Hx_2Si-α-D) is, however, not due to the previously proposed[7] β-hydrogen abstraction from the silene, since it is suppressed in the presence of Et_3SiD. They must originate from Hx_2Si: by intramolecular C–H insertion (see below) either photochemical as in t-Bu_2Si:[15] or more likely thermal.



Consistently an isomer of Hx_2Si: was detected among the products from exhaustive 248-nm irradiation of p-(Hx_2Si) in cyclohexane (GC–MS). These results support the mechanism proposed to account for 308-nm laser-desorption mass spectra of neat poly(dialkylsilanes) in a predominately thermal process.[5] In room temperature solution, Hx_2Si: does not insert into C–H bonds intermolecularly (no Si–D bonds appear upon 248-nm irradiation of p-(Hx_2Si) in cyclohexane-d_{12}).

The wavelength dependence of the silylene extrusion process is unusual. Although exceptions do exist, in organic photochemistry such dependence is usually limited to bichromophoric substrates.[16] Although other explanations cannot be dismissed at this time, it is probably not a coincidence that our results fit naturally into the picture of polysilane photophysics developed previously[7,12] with the INDO/S model[17] to accommodate polarized fluorescence data.

Briefly described it is believed that in room temperature solution the long silicon chain is separated by short kinks (e.g., gauche) into a statistical collection of nearly independent chromophores with an approximately all-trans geometry which are in dynamic equilibrium. The longer the segment the lower its excitation energy, until a limiting value is reached in chromophores with about 10–20 silicon atoms. Thus the coherence length of the singlet excitation is defined by the spacing between sharp twists. Energy transfer from short to longer segments competes with fluorescence.

We now propose that only excitation of the shorter chromophores in the polymer chain up to perhaps Si_7 or so causes silylene extrusion (reaction 1), while excitation of the longer ones does not. The homolytic cleavage reaction (reaction 2) may either occur in both types of chromophores and therefore at all wavelengths or in only the long chromophores. In the latter case, energy transfer from short to longer chromophores would need to be the first step following short wavelength excitation.

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Species-Dependent Biosynthesis of Hyoscyamine

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In 1954[2] it was established that ornithine is a precursor of the tropane moiety of the alkaloid hyoscyamine (**11**) in the plant *Datura stramonium*. In particular, it was shown that [2-^{14}C]-ornithine labeled hyoscyamine at the bridgehead carbons. At that time, the method of degradation used to determine the location of ^{14}C did not distinguish between C-1 and C-5. Later[3,4] it was shown that [2-^{14}C]ornithine is incorporated unsymmetrically, all the ^{14}C being found at the C-1 position (having the R configuration). Studies with a root culture of *Datura stramonium* were complementary to these results.[5] The unsymmetrical incorporation of [2-^{14}C]ornithine into hyoscyamine in root cultures of *Datura metel*[6] was in agreement with the earlier feeding involving intact plants. In this same root culture [5-^{14}C]proline also labeled hyoscyamine unsymmetrically.[7]

In contrast to all these results, it has now been discovered that the radioactive hyoscyamine produced in a root culture of *Hyoscyamus albus L.* which was fed DL-[5-^{14}C]ornithine[8] was labeled equally at the C-1 and C-5 positions. It is thus clear that the biosynthetic pathway between ornithine and hyoscyamine must be different in *Datura* and *Hyoscyamus albus*. This dichotomy of biosynthetic pathways is rationalized in Scheme I. It is proposed that ornithine (**1**) reacts with pyridoxal phosphate (delivered from the complex of ornithine decarboxylase and pyridoxal phosphate) to afford the Schiff base **2**. This compound then

† Corresponding address: Dr. E. Leete Department of Chemistry, 207 Pleasant Street S.E., University of Minnesota, Minneapolis, MN 55455.
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(8) DL-[5-^{14}C]Ornithine·HCl (0.1 mCi, 0.85 mg) was fed to a root culture of *Hyoscyamus albus L.*[9] for 6 days. The harvested roots (fresh wt 67 g) afforded hyoscyamine (25.4 mg) having a specific activity of 2.49×10^7 dpm/mM. The degradation to determine the location of radioactivity is detailed in the Supplementary Material. It is essentially the same as that used previously[2,3,5] with some modifications so that activity at both bridgehead carbons (C-1 and C-5) could be obtained unequivocally.

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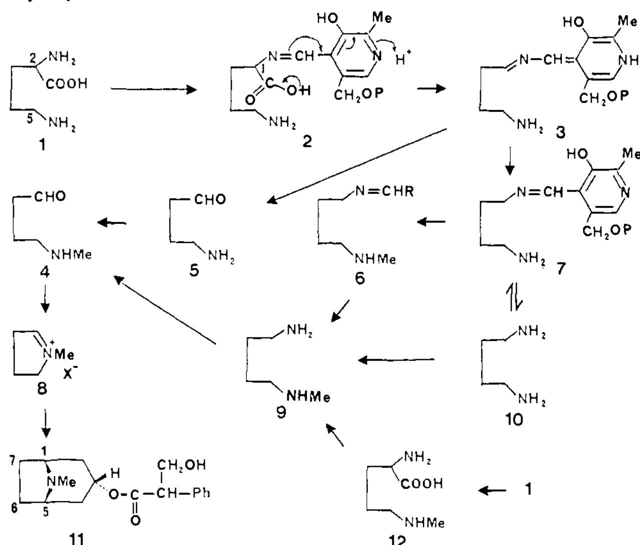
Scheme I. Potential Metabolic Pathways between Ornithine and Hyoscyamine



undergoes decaboxylation as illustrated to yield **3**. A tautomeric shift then affords the Schiff base of putrescine and pyridoxal phosphate (**7**). It is then proposed that this Schiff base undergoes N-methylation to yield **6**. Hydrolysis of this compound yields N-methylputrescine (**9**). Oxidation of **9** catalyzed by the enzyme *N*-methylputrescine oxidase yields 4-(methylamino)butanal (**4**). The cyclized form of this amino aldehyde is the 1-methyl-Δ^1-pyrrolinium salt (**8**), the generally accepted precursor of the tropane skeleton.[10,11] This pathway, as described, will maintain the integrity of C-2 and C-5 of the initial ornithine and will result in unsymmetrical labeling of the tropane nucleus in hyoscyamine derived from [2-^{14}C]ornithine. In support of this pathway *N*-methylputrescine (**9**) has been established as a precursor of hyoscyamine and scopolamine (the 6,7-epoxide of **11**).[12] To explain the symmetrical labeling reported in the present article we propose that the Schiff base **7** undergoes a ready reversible hydrolysis to free putrescine (**10**) before methylation takes place. An alternative route in *Hyoscyamus albus* would be methylation of this free putrescine to *N*-methylputrescine. Indeed the enzyme putrescine-*N*-methyltransferase has been found in *H. albus* root cultures.[13] High levels of radioactivity were also found in putrescine and *N*-methylputrescine after a short (4 h) feeding of [5-^{14}C]ornithine to *H. albus* root culture.[13]

Another explanation of our results was suggested by a referee. It was proposed that the Schiff base **3** undergoes hydrolysis to 4-aminobutanal (**5**) which is then methylated to 4-(methylamino)butanal (**4**). This would be the pathway operating in *Datura*. The incorporation of *N*-methylputrescine observed in *Datura*[12] could be explained by proposing a transamination of this amine to the 4-(methylamino)butanal.

We formerly rationalized the unsymmetrical incorporation of ornithine into hyoscyamine by propsing the intermediate formation of δ-*N*-methylornithine (**12**) which then underwent decarboxylation to yield *N*-methylputrescine. This amino acid was indeed incorporated unsymmetrically into hyoscyamine.[14] It was also detected (by trapping with the unlabeled amino acid) from *Atropa belladonna* plants which had been fed [5-^{14}C]ornithine.[15] However, we have been unable to detect this amino acid in *Datura* species. In *H. albus*, insignificant radioactivity was detected in δ-*N*-methylornithine (added in a trapping experiment) in root cultures which had been fed [5-^{14}C]ornithine. We currently regard δ-*N*-methylornithine as an unnatural compound, its decarboxylation to *N*-methylputrescine being an aberrant reaction. In tobacco this is indeed the case.[16] [2-^{14}C]-δ-*N*-Methylornithine labeled the pyrrolidine ring of nicotine unsymmetrically, whereas [2-^{14}C]ornithine labels the ring symmetrically via free putrescine.[16]

In conclusion, it is clear that the conversion of ornithine to the 1-methyl-Δ^1-pyrrolinium salt (**8**), a precursor of hyoscyamine, can proceed by two pathways, one of which (in *Datura*) cannot involve free putrescine.[17]

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Supplementary Material Available: Full details of the modified degradation scheme of hyoscyamine with the specific activities of the degradation products (4 pages). Ordering information given on any current masthead page. These data will also be provided with requests for reprints.

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Intervalence Enhanced Raman Scattering from $(NC)_5Ru\text{-}CN\text{-}Ru(NH_3)_5^-$. A Mode-by-Mode Assessment of the Franck–Condon Barrier to Intramolecular Electron Transfer

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A key issue in both inter- and intramolecular electron-transfer kinetics is the assessment of vibrational (Franck–Condon) barriers. These barriers arise from redox-induced differences between initial- and final-state normal coordinates or bond lengths. In favorable cases these differences can be determined from X-ray measurements (either EXAFS or X-ray crystal structures) obtained for different oxidation states, and when combined with appropriate force constant (*f*) data, barriers can be directly calculated.[1] In this communication we describe an alternative and potentially more general approach to the Franck–Condon barrier problem, based on an experimental application of time-dependent Raman scattering theory.[2,3] The example we have chosen is optical inter-

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