temperature. Nmr analysis revealed 87.5 and 89.7% vinyl deuteration in two runs, and mass spectral analysis revealed the same extent of total deuteration within experimental error and little or no d_7 species. This means that relatively little bridgehead exchange is taking place.

Semibullvalene (**2**) has only three types of hydrogens (α, β, and γ in a ratio of 4:2:2) as a result of rapid valence tautomerism (eq 1). Hence the two bridgehead hydrogens of vinyl-deuterated barrelene (**3**) will be distributed among the α, β, and γ locations, detectable by nmr, in a way dependent on mechanism. Process I of Chart I requires both of the two hydrogen atoms to appear in the α positions (*i.e.*, 2α, 0β, 0γ). Process II gives the distribution 1α, 0β, 1γ if the final bond formation (note Chart I) is concerted with bond fission and with a preference for bond formation and fission at the same carbon (process IIA). Alternatively, if the preference is for bond formation at the allylic carbon (process IIB), then the distribution 2α, 0β, 0γ is expected. Finally, if the symmetrical allylic biradical **6** has appreciable existence (mechanism IIAB), closures A and B become equally probable except for potential secondary deuterium isotope effects, and the intermediate distribution 1.5α, 0β, 0.5γ should result.

Irradiation of the deuterated barrelene (**3**) in two separate runs, using 50 and 4% acetone in isopentane, afforded semibullvalene (vpc isolation in run 2) with the hydrogen distributions 1.52α, 0β, 0.48γ (run 1) and 1.48α, 0β, 0.52γ (run 2), after correction for residual vinyl hydrogen in the reactant. The uncorrected results along with expected values are collected in Table I.

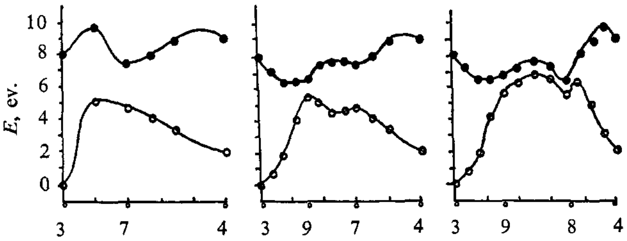
Table I. Summary of Hydrogen Distribution in Semibullvalene Product

Mechanism	Run 1 (12.5% residual vinyl H)			Run 2 (10.3% residual vinyl H)		
	α, %	β, %	γ, %	α, %	β, %	γ, %
I[a]	81.8	9.1	9.1	84.3	7.9	7.9
IIA[a]	50.0	9.1	40.9	50.0	7.9	42.1
IIB[a]	81.8	9.1	9.1	84.3	7.9	7.9
IIAB[a]	65.9	9.1	25.0	67.1	7.9	25.0
Observed	65.5	10.0	24.5	66.5	8.1	25.4

[a] Calculated using known residual vinyl hydrogen content.

The results clearly support mechanism IIAB. No evidence for an appreciable secondary isotope effect is found; this is reasonable in view of the exothermicity of the biradical ring-closure step. Interestingly, the simplest mechanism thus proved not to be correct.

In an attempt to understand the factors controlling the mechanism, the potential energy surfaces of ground and excited states were explored using the general method of Lipscomb and Hoffmann.[5] The results are given for the different mechanisms in Figure 1.



a. Mechanism I b. Mechanism I′ c. Mechanism II

Figure 1. Potential energy *vs.* reaction coordinate for three mechanisms: ○, ground-state curve, ●, excited-state curve.

In the present study Prentice–Hall models were used for each species along the reaction coordinate and the x, y, z coordinates for each carbon and hydrogen atom were obtained by measurement. The drawings in Figure 1 can be considered to be different cross sections of the general potential energy surface leading from reactant barrelene (**1** or **3**) to semibullvalene (**2**, **4**, or **5**).

Mechanism I (Figure 1a) leads on excitation to an electronically excited species requiring an appreciable activation energy (note the minimum available to excited **3** as seen in Figure 1b) to bridge concertedly to give diradical **7**. Interestingly, a slight variation (mechanism I′), in which bridging of the excited state occurs stepwise, circumvents the large barrier; see Figure 1b. However, the main excited-state minimum is positioned above the barrelene surface and vertical demotion should lead back to reactant. The surfaces for mechanism II are such that vertical excitation affords a species with sufficient vibrational energy to surmount the barrier leading to the main excited-state minimum, and this lies above an electronic ground-state minimum which leads preferentially to semibullvalene product. We conclude that this partial exploration of the potential energy surfaces is in accord with the experimental observation of mechanism II.

We also point out that the barrelene to semibullvalene conversion is one example of a general type of excited-state transformation in which a divinylmethane moiety is converted into a vinylcyclopropane group. Some examples are the dibenzobarrelene to dibenzosemibullvalene transformation,[6a] the benzonorbornadiene to tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene reaction,[6b] the 5,5-dimethyl-1,3,6-heptatriene conversion,[6c] the 1,3,6-cyclooctatriene to bicyclo[5.1.0]-2,5-octadiene photolysis,[6c,d] the 1,3-diphenylpropene to 1,2-diphenylcyclopropane irradiation,[6e] and the bicyclo[4.2.2]-2,4,7,9-decatetraene to bullvalene reaction.[6f]

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Atomic Silicon. Reaction with Trimethylsilane

Sir:

Silicon chemistry has been studied by the nuclear-recoil technique employing the reactions ${}^{31}PH_3$ +

neutrons[1] and $Si(CH_3)_4$ + neutrons;[2] the ^{31}Si reactions with the starting materials were reported.

We report here a reaction of thermally vaporized silicon atoms. In an apparatus essentially as described for carbon vaporizations[3] a p-type semiconductor grade of silicon[4] was heated resistively to 1400° *in vacuo* (2×10^{-5} torr) while trimethylsilane was deposited on the liquid nitrogen cooled walls as a trapping agent. Aside from the presence of unidentified products, totaling 5%, the sole reaction product (20–30% based on silicon vaporized) isolated by gas chromatography is 1,1,1,3,3,3-hexamethyltrisilane, ($(CH_3)_3SiSiH_2Si(CH_3)_3$, I). I was identified by analysis of its nmr, infrared, and mass spectra. The nmr spectrum showed two singlets, area ratio 8.85:1, at τ 9.80 and 7.01, respectively, in benzene. The infrared spectra showed absorptions at 3.4, 3.5, 4.8 (Si–H), 7.1, 8.0, 10.9, 11.7–12.0, 13.4, 14.5, and 15.0 μ.

The mass spectrum (70 ev) consisted of a parent peak, *m/e* 176, with P + 1 and P + 2 of expected intensities for three silicon atoms; the $(CH_3)_3Si^+$ peak is the most prominent peak of the spectrum.

The insertion of silicon atoms into the Si–H bond of trimethylsilane is analogous to the earlier reports of insertion into Si–H bonds by carbenes[5,6] and dimethylsilene;[7] it is probably a two-step insertion.

$$(CH_3)_3SiH + Si \longrightarrow (CH_3)_3SiSiH$$

$$(CH_3)_3SiSiH + (CH_3)_3SiH \longrightarrow (CH_3)_3SiSiH_2Si(CH_3)_3$$

The study of silicon atom chemistry with other substrates is in progress.

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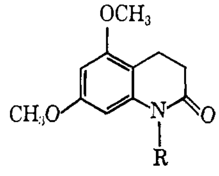
Synthesis of Acronycine

Sir:

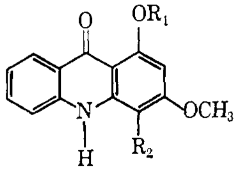
Acronycine,[1–5] an alkaloid isolated from *Acronychia Baueri* Schott, is reported to show significant antitumor activity in experimental animals.[6] We wish to report a synthesis of this natural product.

5,7-Dimethoxy-3,4-dihydrocarbostyril (**1a**, mp 194–195°) is formed in 30% yield by fusing the 3-bromopropionyl derivative of 3,5-dimethoxyaniline with zinc chloride–sodium chloride at 150° for 30 min. Reaction of **1a** with 2-iodobenzoic acid in nitrobenzene with cuprous iodide as the catalyst at 170° for 6 hr yields 1-(2-carboxyphenyl)-5,7-dimethoxy-3,4-dihydrocarbostyril (**1b**, mp 227–229°, 53% yield). Ring closure with polyphosphoric acid at 100° for 2 hr followed by treatment with refluxing 1 *N* methanolic hydrogen chloride for 2.5 hr yields methyl 1,3-dimethoxy-9-oxoacridan-4-propionate (**2a**, mp 244–245°, 83% yield).

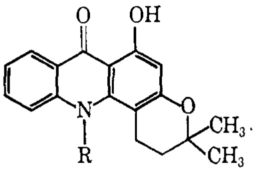
The methoxyl function at C-1 is selectively hydrolyzed with boron trichloride[7] in methylene chloride to form methyl 1-hydroxy-3-methoxy-9-oxoacridan-4-propionate (**2b**, mp 194–195°, 80% yield). Treatment of **2b** with excess methyllithium in tetrahydrofuran at −20° gives the corresponding tertiary carbinol **2c** (mp 213–214°, 82% yield). Fusion of **2c** with pyridine hydrochloride at 200° for 2 hr yields 6-hydroxy-3,3-dimethyl-2,3-dihydro-7(12H)-1H-pyrano[2,3-*c*]acridinone (**3a**, mp 278–280° dec). Owing to its tendency to crystallize on the column during silica gel chromatography, **3a** is not ordinarily isolated. Instead, the crude product is allowed to react with methyl iodide and potassium carbonate in refluxing acetone[2] to give nordihydroacronycine (**3b**, mp 213–215°, 20% over-all yield). This compound is identical by the usual physical comparisons with an authentic sample prepared from acronycine.[2]



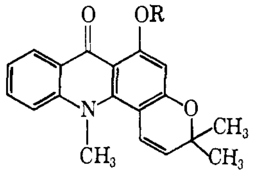
1a, R = H
b, R = 2-HOOCC$_6$H$_4$



2a, R$_1$ = CH$_3$
R$_2$ = CH$_2$CH$_2$COOCH$_3$
b, R$_1$ = H
R$_2$ = CH$_2$CH$_2$COOCH$_3$
c, R$_1$ = H
R$_2$ = CH$_2$CH$_2$C(CH$_3$)$_2$OH



3a, R = H
b, R = CH$_3$



4a, R = H
b, R = CH$_3$

Alternately, **3a** is prepared by treating 1,3-dihydroxy-9-acridanone,[8] prepared by hydrolysis of 1,3-dimethoxy-9-acridanone,[3] with 3,3-dimethylallyl chloride and zinc chloride in refluxing trifluoroacetic acid for 3 hr (18% yield).

Conversion of **3b** to noracronycine (**4a**) is accomplished with 2,3-dichloro-5,6-dicyanobenzoquinone in refluxing toluene (40% yield). The product obtained is identical with an authentic sample prepared from the natural product.[2] Methylation of **4a** to

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