

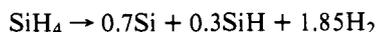
excess C_2H_4 (used as a free radical trap and chain suppressor) and have concluded that both dissociations are initiated by H_2 molecular elimination reactions like reaction 1. They also report Arrhenius parameters for H_2 elimination consistent with intrinsic activation entropies of, $\Delta S^\ddagger = 3.7 \pm 0.4$ eu/mol. Assuming this intrinsic activation entropy for the silylene molecular H_2 elimination reaction gives $A_1 = 10^{15.2} s^{-1}$. We have performed RRKM pressure falloff calculations for a transition-state model consistent with this high pressure A factor and with a rate constant of $k_1 = 1.86 \times 10^4 s^{-1}$ at 1304 K, $P = 3825$ Torr. The calculations indicate that reaction 1 is in its falloff region with $k/k_\infty = 0.32$ and give a high pressure activation energy of 61.7 kcal/mol and a critical activation energy of $E_0 = 59.1$ kcal/mol. We are presently refining our shock tube data using the internal standard comparative rate technique⁶ and should soon be able to report firm values for the Arrhenius parameters of reaction 1.

Results for SiD_4 pyrolysis in the presence of excess toluene (Table I) conclusively show that the D atoms generated in the SiD_4 decompositions under shock conditions arise from the fast dissociation of SiD_2 :



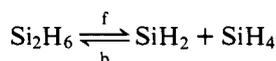
Thus under the conditions stated (i.e., large toluene excess) there was no significant change in reaction rates (hence no appreciable chain-induced SiD_4 decomposition), and all D atoms generated should be scavenged by toluene to give HD. The observation of significant amounts of HD and D_2 requires a molecular elimination reaction for D_2 production (reaction 1) and a D atom generation reaction. The latter process must be reaction 3 since reaction 2 is far too slow. Further, the nearly 1:1 D_2 :HD ratios observed⁷ suggest nearly complete dissociation of SiD_2 at shock temperatures. If the SiD_2 dissociation were not complete, one would expect a change in the ratio of hydrogen produced to silane consumed with increasing temperature. However, our stoichiometric data indicate that this ratio remains constant within experimental error from 1200 to 1300 K: $\Delta(H_2)/\Delta(SiH_4) = 1.85 \pm 0.10$. Therefore, the first two steps of the shock tube dissociation of silane are reactions 1 and 3, respectively.

Since no disilanes or higher silanes were found in the mass spectra of the products, the reaction stoichiometry is reasonably well represented by



suggesting a significant amount of $SiH + H \rightarrow H_2 + Si$ in uninhibited shock pyrolyses.

An analysis of reactions 1 and 3 by the usual kinetics of consecutive reactions⁸ provides a lower limit for k_3 . Thus the stoichiometry establishes an upper limit for SiH_2 formation: (SiH_2 produced/ SiH_4 initial) ≤ 0.15 . With 80% SiH_4 dissociated, one then calculates $k_3/k_1 \leq 2.2$ at 1304 K. Also, assuming $A_3 \approx 10^{14.0} s^{-1}$, an upper limit of $E_3 \leq 56.0$ kcal/mol is obtained. This surprisingly low value leads to the interesting thermochemical values below, using $\Delta\bar{H}_f^\circ(SiH_4) = 8.2$ kcal/mol,⁹ $\Delta\bar{H}_f^\circ(Si_2H_6) = 17.0$ kcal/mol,⁹ $\Delta\bar{H}_f^\circ(Si) = 107.7$ kcal/mol,⁹ BDE(SiH_3-H) = 94 kcal/mol,¹⁰ and for the reaction



$E_f = 49.3$ kcal,¹¹ $E_b = X$. BDE(2): $SiH_3 \rightarrow SiH_2 + H$ ($\Delta H^\circ = 60.1 - X$, $\Delta\bar{H}_f^\circ(SiH_3) = 50.1$ kcal/mol, $\Delta\bar{H}_f^\circ(SiH_2) = (58.1 - X)$ kcal/mol). DBE(3): $SiH_2 \rightarrow SiH + H$ ($\Delta H^\circ = 56.0$ kcal, $\Delta\bar{H}_f^\circ(SiH) = (62.0 - X)$ kcal/mol). BDE(4): $SiH \rightarrow Si + H$ ($\Delta H^\circ = 97.8 + X$ kcal).

It is interesting to compare the RRKM-calculated value of the rate constant for reaction at the static pyrolysis conditions

of Purnell and Walsh,¹ with their observed rate constants. Thus at 653 K, with $[SiH_4] = 3.2 \times 10^{-3}$ M (i.e., ~ 100 Torr), the Purnell and Walsh results give for a first-order rate constant $k_{uni} = 10^{15.18 - (55.91/\theta)} \times [SiH_4]^{1/2} = 1.7 \times 10^{-5} s^{-1}$. The RRKM-calculated value is $k_1 = 3.7 \times 10^{-7} s^{-1}$, with $k/k_\infty \approx 0.11$. The observed rate constant is therefore more than a factor of 40 larger than the initiation rate constant, k_1 . This supports the view that the pyrolysis under static system conditions follows predominantly a chain mechanism.² We are presently refining our shock tube kinetic data, reexamining the reaction under static low temperature conditions, and completing the RRKM calculations on the reaction falloff properties.

Acknowledgment. We thank Professor David Lewis and Peter Jeffers for their advice on the construction and operation of our shock tube.

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- (4) From transition-state theory, $A = (ekT/h)\rho^{\Delta S^\ddagger/h}$ and $\Delta S^\ddagger = \Delta S^\ddagger_{intrinsic} + R$ ln (reaction path degeneracy, rpd). For the silane dissociation, $\Delta S^\ddagger_{intrinsic} > 0$ and rpd = 6; therefore $A \geq 10^{14.4} s^{-1}$.
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Stereospecific Total Synthesis of *dl*-Helenalin: A General Route to Helenanolides and Ambrosanolides

Sir:

Helenalin (**1**), a potent cytotoxic substance¹ isolated from *Helenium autumnale* over 65 years ago,² is representative of a group of pseudoguaianolides known as helenanolides,³ which have as a characteristic feature a C-10 α -oriented methyl group. Despite early attempts at structure elucidation,^{4,5} it was not until the early sixties that the relative and absolute configuration of **1** was established.^{6,7}

We have reported⁸ the facile and efficient synthesis of intermediate **3** in 25% overall yield from norbornadiene and

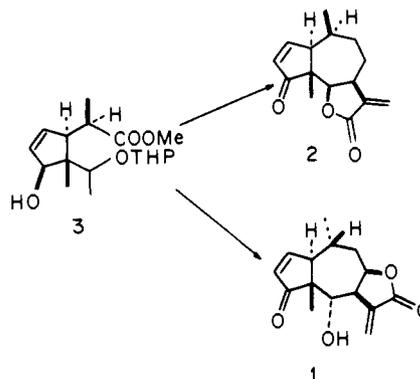
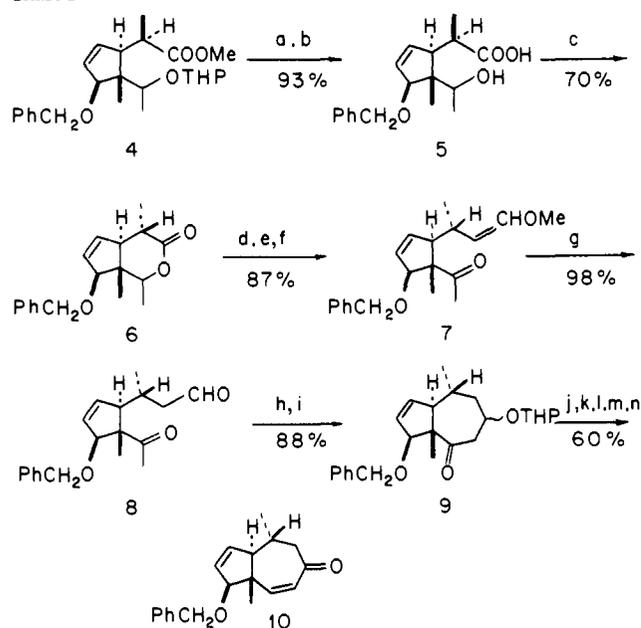
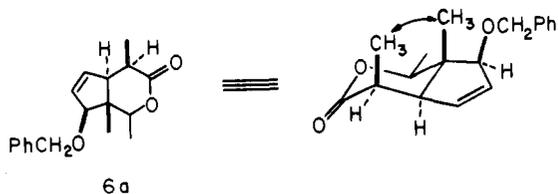


Chart I^a

^a a, MeOH, TsOH; b, KOH, EtOH-HOH (6:1), reflux, 20 h; c, DBU (3.0 equiv), TsCl (1.3 equiv), PhCH₃, 25 °C (30 min) → reflux; d, *i*-Bu₂AlH, PhCH₃, -78 °C; e, Ph₃P⁺CH₂OMeCl⁻, *t*-AmONa, PhH, 1.5 h; f, CrO₃·2Py, CH₂Cl₂, 0 °C, 45 min; g, 10% HCl, THF; h, 1.5% KOH in MeOH; i, DHP, TsOH, 0 °C; j, NaBH₄, EtOH, 0 °C; k, MsCl, Py, 0 °C; l, MeOH, TsOH, 0 °C; m, Jones; n, DBU (3.0 equiv), PhH, 45 min.

described⁸ its conversion into ambrosanolides (e.g., ambrosin (**2**) and damsin) which have the C-10 methyl group β oriented.^{9,10} We now detail the transformation of **3** into *dl*-helenalin (**1**), thus demonstrating the ability of cyclopentenol **3** to function as a *common synthetic intermediate for both the helenanolides and ambrosanolides*.

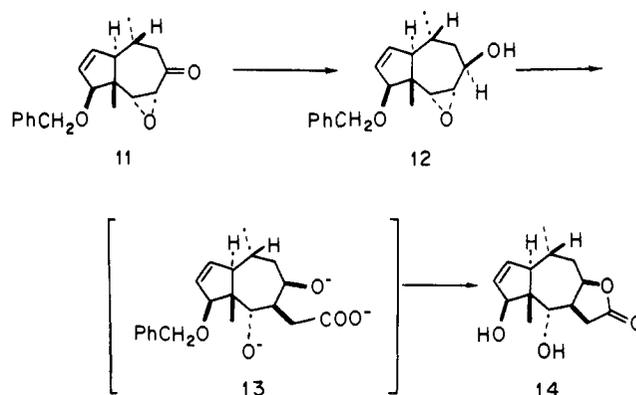
The construction of hydroazulenone **10** possessing the C-10 α -oriented methyl group is illustrated in Chart I. Benzylation of cyclopentenol **3** was carried out at reflux in 81% yield employing sodium hydride (1.5 equiv) in tetrahydrofuran containing benzyl bromide (1.5 equiv) and hexamethylphosphoramide (1.0 equiv), all in the presence of tetra-*n*-butylammonium iodide.¹¹ Cleavage of the tetrahydropyranyl ether **4** and hydrolysis of the methyl ester provided hydroxycarboxylic acid **5**. Treatment of **5** with *p*-toluenesulfonyl chloride and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in toluene generated exclusively lactone **6** in 70% yield. The complete isomerization of the methyl group is not surprising in view of the severe 1,3-diaxial methyl-methyl interaction which exists in the initially produced lactone **6a**. Reduction of lactone **6** with



diisobutylaluminum hydride provided the corresponding lactol which upon reaction with methoxymethylenetriphenylphosphorane (generated in benzene with sodium *tert*-amylate) and subsequent Collins oxidation afforded keto enol ether **7** (87% overall). Hydrolysis of the enol ether generated keto aldehyde **8**: IR (CCl₄) 1728, 1702 cm⁻¹; NMR (CCl₄) δ 9.67 (s, 1 H, -CHO), 2.15 (s, 3 H, CH₃CO-). Intramolecular aldol condensation of keto aldehyde **8** provided the corresponding aldol in high yield which *without purification* was directly tetrahydropyranylated providing the protected aldol **9**. The

required hydroazulenone **10** (mp 79–80 °C; IR (CCl₄) 1675 cm⁻¹; NMR (CCl₄) δ 6.50 (d, 1 H, *J* = 12 Hz), 5.82–5.95 (m, 3 H)), was prepared from **9** in 60% overall yield via the sequence of reactions outlined in Chart I.

With the hydroazulene skeleton in hand we focused our efforts on the elaboration of the C-6 α -hydroxyl and the C-7,C-8 β -oriented α -methylene- γ -butyrolactone unit. Epoxidation¹² of enone **10** with *tert*-butyl hydroperoxide in tetrahydrofuran containing Triton B gave in 93% yield the crystalline α -epoxy ketone **11**, mp 60–61 °C, as the sole product. It was anticipated that the bulky *tert*-butyl hydroperoxide anion would approach the enone system from the side opposite the C-5 methyl group. Reduction of epoxy ketone **11** with so-



dium borohydride in ethanol (0 °C, 30 min) gave exclusively in near-quantitative yield epoxy alcohol **12**, mp 90–91 °C.

Despite the hindered nature of C-7, epoxide **12** was treated with 14.7 equiv of dilithioacetate¹³ in dimethoxyethane at 55 °C for 22 h followed by the addition of the resultant trianion **13** to a solution of lithium in liquid ammonia. Quenching of the reaction with solid ammonium chloride after 1.0 min and workup with aqueous hydrochloric acid (pH 3) provided exclusively the crystalline tricyclic lactone **14** (mp 162–164 °C; IR (CHCl₃) 1768 cm⁻¹) in 86% overall yield.

α -Methylenation was performed on the corresponding bis-(tetrahydropyranyl) ether (prepared in 82% yield from **14** (dihydropyran, *p*-toluenesulfonic acid, methylene chloride, 0 °C, 1.5 h) via the sequence (1) hydroxymethylation¹⁴ (-20 °C), (2) mesylation (0 °C, 1 h), and (3) β -elimination (DBU, benzene, 1 h) in 61% overall yield. Removal of the protecting groups (60% acetic acid, 45 °C, 3 h) gave (78%) a crystalline diol, mp 157–158 °C, which upon oxidation with manganese dioxide in methylene chloride-benzene (1:2) provided (69%) after chromatography on SilicAr CC-7 pure crystalline *dl*-helenalin (**1**), mp 225–228 °C, identical in all respects with an authentic sample of natural helenalin by comparison of spectral properties (IR, NMR, mass spectrometry) and thin-layer mobility in several solvent systems.

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Nonselective Proton Transfer from *p*-Cymene as the Radical-Cation Half of an Exciplex

Sir:

Several years ago we demonstrated that the photoreduction of α,α,α -trifluoroacetophenone (AF₃) with reductants such as toluene and cumene proceeds via charge transfer followed by proton transfer from aromatic to ketone.¹ This mechanism is analogous to that for the photoreduction of ketones by amines.² Since the reductants assume radical-cation character in the charge transfer (exciplex) intermediate, there is the possibility that reductants possessing more than one kind of activated hydrogen might show unusual relative proton labilities. Such selectivities have not been measured heretofore in aprotic media; we report the first example in this paper.

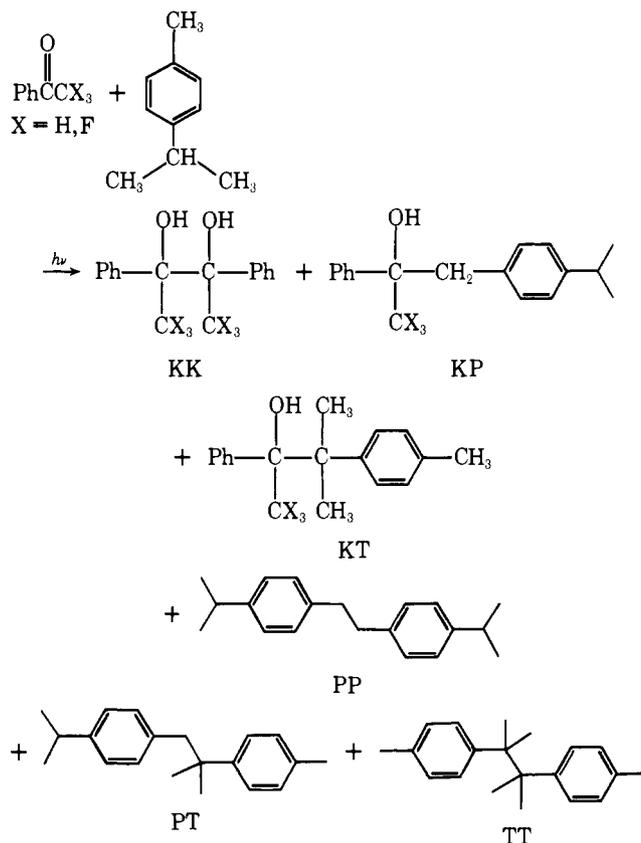
Irradiation of either acetophenone, AH₃, or AF₃ in *p*-cymene produces the expected six radical coupling products: three hydrocarbons, two alcohols, and the pinacol. These products account for over 80% of the reacted ketones and only traces of other products were detectable by VPC analysis. The hydrocarbons were separated from the other products by vacuum distillation and from each other by sublimation. With AH₃, the bicumyl TT³ was the major radical coupling product, whereas with AF₃ the bibenzyl PP was the major product. Product ratios were independent of conversion and of cymene concentration (0.1–0.6 M for AF₃, 0.75–2.5 M for AH₃) and were comparable in either benzene or acetonitrile as solvent. Table I lists representative quantum yields.

With AF₃, the KP/KT ratio averages 3.4; the (PP/TT)^{1/2} ratio averages 3.2; and the total P/T ratio in the three hydro-

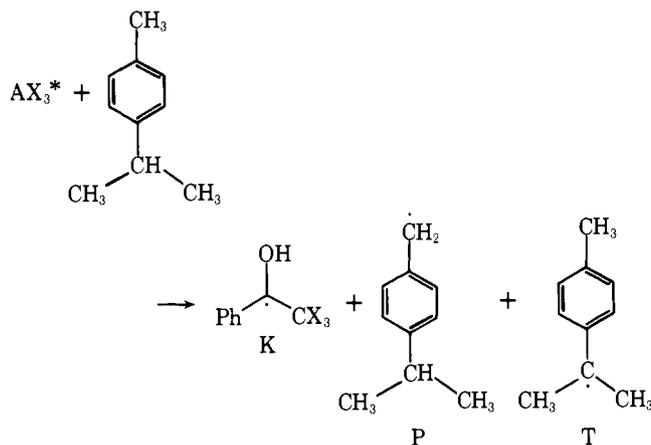
Table I. Product Quantum Yields in the Photoreduction of Acetophenone and Trifluoroacetophenone by Cymene^a

product	PhCOCF ₃ ^b	PhCOCH ₃ ^c
TT	0.0014	0.012
TP	0.0065	0.008
PP	0.0130	0.002
KT	0.013	<i>d</i>
KP	0.043	<i>d</i>

^a 313-nm excitation, 25 °C, benzene solvent. ^b 0.6 M *p*-cymene. ^c 2.5 M *p*-cymene. ^d Not yet determined.



carbons averages 3.4. We can therefore conclude that the benzylic radicals P and T are formed in 3.4:1 ratio. Moreover,



the ketyl radicals do not preferentially react with one or the other benzyl radical. If we assume that the ketyl radicals from AH₃ behave likewise, the hydrocarbon product ratios from AH₃ indicate that P and T are formed in a 1:2.6 ratio.

The preference for tertiary radical formation with AH₃ is expected for direct hydrogen atom abstraction⁵ and agrees closely with the 2.4-fold greater reactivity toward triplet AH₃ of cumene relative to toluene.¹

The 3.4-fold preference for primary over tertiary radical formation with AF₃ is unprecedented and does not parallel the 1.7-fold greater reactivity toward triplet AF₃ of toluene relative to cumene. In fact, a standard double reciprocal plot⁶ of product quantum yield as a function of cymene concentration indicates that *p*-cymene reacts with triplet AF₃ with the same rate constant as does *p*-xylene, $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, 14 times faster than does toluene.¹ Product ratios are not coupled with rates of reaction with triplet ketone because of the intervention of a CT complex (triplet exciplex).¹ Benzyl radical formation involves transfer of an electron-deficient hydrogen from