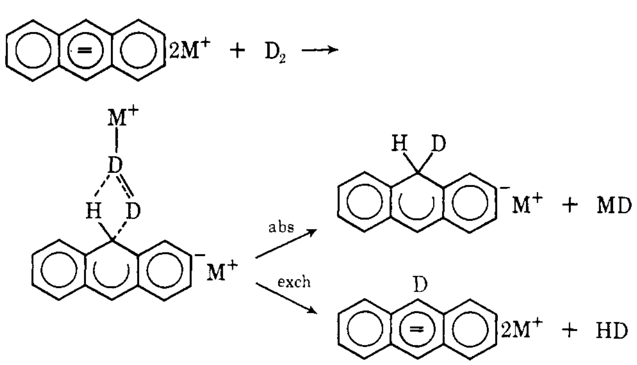

complex formation, relative to the formation of complexes of Na and Li.

Similar different behavior of the different alkali metals was observed in other EDA complexes such as naphthalene, phenanthrene, and pyrene.

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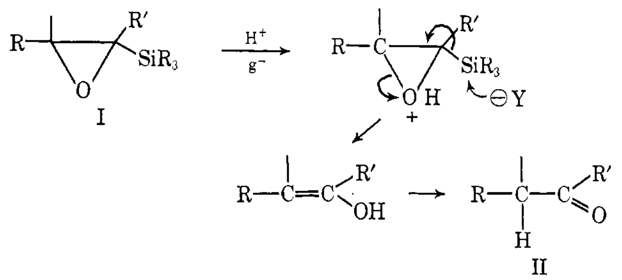
A New Synthesis of Aldehydes *via* Vinylsilanes

Sir:

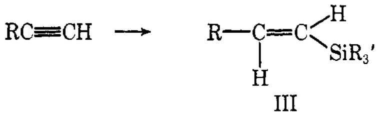
We describe a new synthesis leading to aldehydes (and ketones).

The synthesis was designed on the assumption that the well-known propensity of suitably substituted organosilanes toward β elimination[1] should result in the transformation of epoxysilanes into carbonyl compounds, as shown in I → II. This has now been shown to be the case.

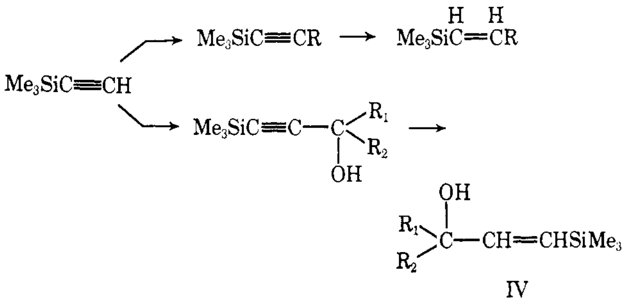


Epoxysilanes (*cf.* I) have been described previously.[2] They are easily made by epoxidation of the corresponding ethylene derivatives which can themselves be prepared easily (when R′ = H),[3] either by the addition of trialkysilanes to terminal acetylenes in the presence of chloroplatinic acid[4] (Scheme I), or by the alkylation of organometallic derivatives of the easily available trimethylsilylacetylene[5] followed by semihydrogenation (Scheme II).

Scheme I

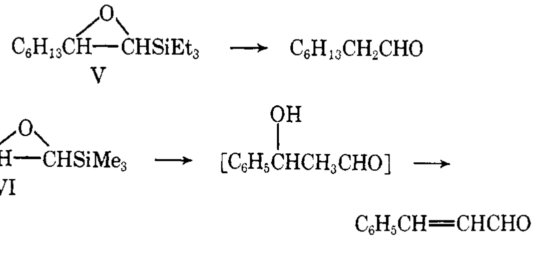


Scheme II



The complete sequence is illustrated by the transformation of 1-octyne to octanal and of benzaldehyde to cinnamaldehyde. Addition of triethylsilane (100% excess) to 1-octyne (100°, 5 hr, 2 drops of 10% H_2PtCl_6 under N_2) gave a 90% yield of *trans*-1-octenyltriethylsilane (III, R = C_6H_{13}; R′ = C_2H_5): bp 128–132° (6 mm); λ_{max}^{film} 6.18, 8.1, 9.85, 12.8, and 13.6–13.9 μ; δ (neat) 0.3–1 (m, 18 H) 2.2 (m, 2 H), 5.55 (d, J = 18 Hz, 1 H), 6.13 (d of t, J_1 = 18 Hz, J_2 = 6 Hz, 1 H). Epoxidation with *m*-chloroperbenzoic acid in methylene chloride at room temperature overnight gave the corresponding epoxide V: bp 98° (0.8 mm); λ_{max}^{film} 8.05, 9.85, and 13.5–13.9 μ; δ (CCl_4) 0.3–1 (m, 18 H), 1.88 (d, J = 4 Hz, 1 H), 2.7 (broad d, J = 4 Hz, 1 H). Treatment of the epoxide with 2,4-dinitrophenylhydrazine reagent gave a 65% yield of the 2,4-dinitrophenylhydrazone of octanal, mp 105.5–106° (lit.[6] 106°).

Treatment of the epoxysilane with a solution of 1 ml of sulfuric acid in 10 ml of methanol at 90° for 10 min, followed by work-up, gave a 60% yield of octanal as its dimethyl acetal: λ_{max}^{film} 8.8, 9.2–9.5, and 10.4 μ; δ (CCl_4) 3.2 (s, 6 H), 4.25 (t, J = 5 Hz, 1 H), 0.9 (broad s, 3 H), and 1.35 (broad s, 12 H). Hydrolysis with aqueous acetic acid again gave octanal.



Similarly, 1-(3-hydroxy-3-phenylpropenyl)trimethylsilane (IV, R_1 = C_6H_5; R_2 = H) was prepared by the reaction of the chloromagnesium salt of trimethylethynylsilane with benzaldehyde in ether (6-hr heating), followed by semihydrogenation in ethyl acetate with 10% palladium/charcoal, in the presence of some pyridine. The resulting mixture of olefins (largely cis)

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(3) The synthesis and use of vinylsilanes where R′ = CH_3 (leading to methyl ketones) are reported in G. Stork and E. Colvin, *J. Amer. Chem. Soc.*, in press.

(4) *Cf.* R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, **83**, 4385 (1961).

(5) L. Q. Minh, J. C. Billiotte, and P. Cadiot, *C. R. Acad. Sci.*, **251**, 730 (1960); *cf.* R. West and L. C. Quass, *J. Organometal. Chem.*, **18**, 351 (1969).

(6) C. F. H. Allen, *J. Amer. Chem. Soc.*, **52**, 2955 (1930).

was epoxidized with *m*-chloroperbenzoic acid as before, to produce the epoxide VI in about 58% overall yield from benzaldehyde. Treatment of the epoxide with methanolic sulfuric acid (*vide supra*) produced cinnamaldehyde in about 70% yield.

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Singlet Quenching Mechanisms

Sir:

Charge-transfer interactions have been shown to be the predominant quenching mechanism for the singlet states of aromatic compounds with amines,[1-4] carbon tetrachloride,[2] and quadricyclene.[5] The mechanism of fluorescence quenching of the azo compounds 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO)[6,7] and 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH)[6,7] and aromatic hydrocarbons[8] has been described as exciplex-induced radiationless decay.[7,8] We have found that minor modifications of the normal Stern–Volmer equation allow testing of the various mechanisms for singlet quenching. We would like to present evidence that the major quenching interaction for fluorescence quenching of the azo compounds and aromatic hydrocarbons is also charge transfer.

The usual scheme for fluorescence quenching reactions is written

$$A^s + Q \xrightarrow{k_q'} (AQ)^*$$

in which k_q' is the apparent rate of quenching of the excited molecule A^s by the substrate Q. This mechanism leads to the normal Stern–Volmer equation

$$\phi_0/\phi = 1 + k_q'\tau_s[Q] \qquad (1)$$

where ϕ_0 and ϕ are the quantum yields for fluorescence in the absence and presence of the quencher and τ_s is the lifetime of the singlet state of A. However, a slightly different scheme for diffusion-controlled reactions has been presented by North.[9] It is, as written for fluorescence quenching by electron transfer

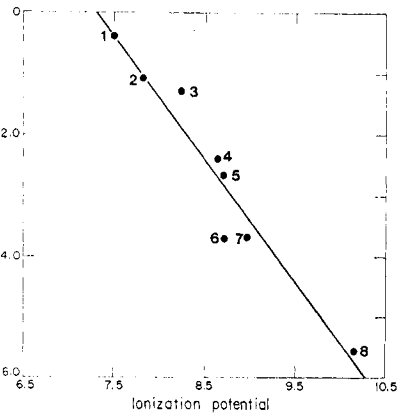

Figure 1. Fluorescence quenching of acridine: (1) triethylamine (IP = 7.50 eV[11a]), (2) trimethylamine (IP = 7.82 eV[11a]), (3) dimethylamine (IP = 8.24 eV),[11a] (4) benzylamine (IP = 8.64 eV[11a]), (5) *n*-butylamine (IP = 8.71 eV[11a]), (6) isopropylamine (IP = 8.72 eV[11a]), (7) methylamine (IP = 8.97 eV[11a]), (8) ammonia (IP = 10.19 eV[11a]). The least-squares procedure gives the empirical equation, $\ln [k_q'/q(k_{diff} - k_q')] = 14.9 - 2.03\text{IP}$, with k_{diff}(water) $= 7.38 \times 10^9$ l. mol^{-1} sec^{-1}, with a correlation coefficient of 0.966.

$$A^s + Q \underset{k_{-q}}{\overset{k_{diff}}{\rightleftharpoons}} (A^s|Q) \xrightarrow{k_r} (\overset{-}{A}{}^0\overset{+}{Q}{}^0)$$

where k_{diff} is the rate constant for the diffusion of A^s and Q to form the proximity pair $(A^s|Q)$, k_{-q} is the rate constant for diffusion of the proximity pair out of the solvent cavity, and k_r is the rate constant for the quenching reaction. This leads to the Stern–Volmer equation

$$\phi_0/\phi = 1 + [k_{diff}k_r/(k_{-q} + k_r)]\tau_f[Q] \qquad (2)$$

It can be seen from eq 1 and 2 that $k_q' = k_{diff}k_r/(k_{-q} + k_r)$. Since k_q' can be measured and k_{diff} calculated, the ratio k_r/k_{-q}, which is given by

$$k_r/k_{-q} = k_q'/(k_{diff} - k_q')$$

can be determined. If we assume that the rate constant for diffusion out of the solvent cavity, k_{-q}, is to the first approximation determined by only the properties of the solvent, then

$$\ln (k_r/k_{-q}) = \left(\ln \frac{k_q'}{k_{diff} - k_q'}\right) \propto \Delta G^{\pm}$$

where $\Delta G^{\pm}$ is the free energy of activation for the electron-transfer reaction. For a constant fluorescer and a series of quenchers,[1,3,4,5,10] $\Delta G^{\pm} \propto \text{IP} + C$, where IP is the ionization potential of the donor and C is comprised of a series of terms related to the solvation of a pair of ions.

In Figure 1 the function $\ln [k_q'/(k_{diff} - k_q')]$ is plotted *vs.* ionization potential for the amine quenching of acridine,[4] a known example of charge-transfer quenching. (IP values given in the figure captions are taken from ref 11.) The linear behavior indicates

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