obtained for high energy irradiations in glycerol water media may arise from either or both of two plausible mechanisms: (1) there may be a relatively low energy onset of a CTTM state corresponding to photo-oxidation of solvent glycerol or (2) the shape of excited state potential energy surface, the binding energy of the CTTM excited state, etc., are to a significant extent functions of the solvent environment of complex ion substrate. Actually the first "alternative" is a limiting case of the second since CTTM excitation results in an inward flow of negative charge in the solvated complex. Clearly the Franck-Condon state (1CT*) reached in the initial excitation must have ground state (1A) solvation, and this solvent environment must ultimately relax to solvation appropriate to the radical pair products ([Co(NH₃)₅⁺, X]); eq 1-3 describe the proposed sequence of events, where the excited state 1CT could in principle differ from 1CT* in thermal equilibration and also in spin multiplicity. It is to be observed that (1) describes an electronic transition with a large electric dipole moment, so that (1-3) would require a large adjustment in the solvent environment. We are proposing therefore that the solvent plays a more active role in CTTM photochemistry of transition metal complexes than has been previously suspected and that photo-physical processes affecting the quantum yield, processes such as electronic relaxation, intersystem crossing, etc., can occur within the lifetime of the CTTM states (1CT*, 1CT, or other states populated along the coordinate for reaction 2).

Figure 1. Absorption spectrum (upper curve) and quantum yields of Co²⁺ (lower curves) from ultraviolet irradiations of Co(NH₃)₅⁻ NCS⁺. For lower set of curves quantum yields were obtained in water (solid circles) or 50% glycerol-water (open circles) solutions; activation energies (solid squares) were obtained from quantum yields obtained from irradiations of aqueous solutions in the range 25-60°. Dotted portion of the curve for activation energies is drawn in accord with the report in ref 2b of an activation energy for irradiations at λ > 450 nm.

approximately zero for 254-nm irradiations. The prominent absorption feature in this spectral region, the band at 305 nm, may be a ligand centered transition. The above observations suggest vibrational equilibration within the corresponding excited state, followed by competitive electronic relaxation to the ground state (or at least to a less reactive lower energy excited state; this complex is not very photosensitive to ligand field excitation and population of a reactive charge transfer excited state. It is most significant that for this complex the decreased values of ϕ₀⁺ in glycerol are associated with an increased thermal activation barrier and that contrasting behavior was found for higher energy excitations. Since the medium viscosity must decrease as temperature increases, these observations again imply that while competitive diffusive and recombination processes of radical pair products may be a feature of the sequence of events following excitation in the 350-280-nm range they cannot be dominant mechanistic features for the higher energy excitations. The unexpectedly high yields of Co²⁺ which we have

Vinylsilanes as Carbonyl Precursors.

Use in Annellation Reactions

Sir:

The addition of a 3-ketoalkyl chain α to a carbonyl function, an important step in annellation reactions, requires either Michael addition to a suitable vinyl ketone or alkylation with a 3-ketoalkyl halide equivalent. The latter process is in principle the more general. Maximum versatility, including the important possibility of using the halide in trapping regiospecifi-

cally generated enolates, requires that the halide be especially reactive, e.g., a benzylic or allylic halide. The isoxazole annelation sequence belongs to the benzyl type halide, while suitable allylic halides have to be of type 1 in which the substituted vinyl system A—

\[
\begin{align*}
\text{A} & \quad \text{C}=\text{CHCHX} \quad \text{RCHC}=\text{CCH=CHC} \\
\text{R} & \quad \text{C} \quad \text{H} \\
\end{align*}
\]

C—C must be compatible with reasonable stability of 1 as well as easy transformation to the required carbonyl function.

We have previously shown that epoxysilanes such as 2 are converted into acetals by refluxing with methanolic sulfuric acid, thus demonstrating the potential of the vinylsilane function as a latent carbonyl.

We now describe the extension of this concept to annelation reactions. We first demonstrate the suitability of the silylallyl halides in various types of alkylation reactions and then show that the alkylation products can be transformed under unusually mild conditions into the 1,5- and 1,4-diketone precursors of the desired cyclohexenones and cyclopentenones.

Alkylation of the lithium enolate 3, kinetically generated from its enol acetate, took place readily with 1 equiv of the iodide 4 (tetrahydrofuran, room temperature) to give 5 (91% yield): bp 45° (0.02 mm); nmr (CCl₄) δ 5.51 (1H, t, J = 7 Hz, of HC=C), 0.98 (3H, s, CH₃), 0.00 (9H, s, C₂H₅Si); mass spectrum m/z 232, 223, 112, 73.

The synthetically very important trapping of enolates regiospecifically produced by lithium reduction of enones was demonstrated starting with testosterone (6): addition of an ether solution of testosterone in 50 ml of ether to a solution of 3 equiv of lithium in anhydrous liquid ammonia (final ratio tetrahydrofuran : ether 2 : 1) gave after 5 hr at room temperature, the alkylated cyclohexanone 8 in 75% yield after silica gel chromatography (60:40, hexane: methylene chloride). The structure follows from its conversion to the methyloctalone 15 (vide infra).

It is worth noting that, although the sequence lithium reduction—enolate trapping is often more satisfactory than enone alkylation followed by reduction, it is possible to reduce unsaturated enones without affecting the potentially reducible vinylsilane system. The octalone 9 prepared in 85% yield by alkylation of the pyrrolidine enamine of Δ¹,2-octalone with 4 was reduced to 10 in essentially quantitative yield with 3 equiv of lithium in liquid ammonia—tetrahydrofuran (3:1) containing 1 equiv of tert-butyl alcohol.

Release of the ketonic function latent in the vinylsilane system could be effected with remarkable ease. It will be recalled that simple epoxysilanes require refluxing with 10% methanolic—sulfuric acid for this transformation. We also found that similar conditions were required for the transformation of the simple epoxysilane (made by chloroperbenzoic acid-catalyzed addition of triethylsilane to 4-octyne, followed by m-chloroperbenzoic acid in methylene chloride) to 4-octanone. It is especially worth noting that 11 was

\[\text{(1)} \quad \text{G. Stork, S. Danishefsky, and M. Ohashi, J. Amer. Chem. Soc., 89, 5459 (1967); G. Stork and J. E. McMurry, ibid., 89, 5463, 5464 (1967).} \]

\[\text{(2)} \quad \text{G. Stork and E. Colvin, J. Amer. Chem. Soc., 93, 2080 (1971).} \]


\[\text{(4)} \quad \text{The synthesis of the silylated alkylation halides used in this paper is described in the accompanying paper: G. Stork, M. Jung, E. Colvin and Y. Noel, J. Amer. Chem. Soc., 96, 2664 (1974).} \]

\[\text{(5)} \quad \text{Satisfactory nmr, ir, and mass spectral data were obtained for all new compounds reported. Chloroform (δ 7.74) was used as an internal standard for the nmr spectra of compounds containing the trimethylsilyl group.} \]


\[\text{(7)} \quad \text{For the trapping of enolates from cuprate addition, see G. Stork, Pure Appl. Chem., 17, 1381 (1968).} \]


\[\text{(9)} \quad \text{Cf. E. Y. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements," Consultants Bureau, New York, N. Y., 1966.} \]

\[\text{Communications to the Editor} \]
unaffected by formic acid at room temperature or by heating with acetic acid in ethanol.

In startling contrast, while treatment of the ketonic vinylsilane 5 in methylene chloride with a slight excess of m-chloroperbenzoic acid at 0° for 10 min gives largely the epoxysilane 12, further keeping of the reaction mixture for 4 hr at room temperature led, in 90% yield, to the known dione 13,10 cyclized under the usual basic conditions to the octalone, identical with an authentic sample.

The transformation of the epoxysilane 12 to the dione 13 is evidently brought about merely by the m-chloro-benzoic acid formed in the epoxidation. Isolated epoxide 12 is also transformed into 13 by shaking with formic acid for 30 sec (contrast the stability of 11 under these conditions).

We believe that the extreme ease of the transformation epoxysilane → ketone in this and similar cases (side infra) strongly suggest nucleophilic participation of the carbonyl group in the epoxide opening, in a manner reminiscent of the carbonyl participation involved in the directed hydration of certain ketoacetylenes to 1,4- and 1,5-diketones.11 A related mechanism is outlined for the 12 → 13 transformation.

Under similar conditions, the vinylsilane 8 was transformed (final treatment with formic acid) to the dione 14 (83% yield), further cyclized in 82% yield (3 M potassium hydroxide in ethanol) to 5-methyl-Δ 1,5,2-octalone (15) identical with an authentic sample made by Birch reduction of the known 12 5-methyl-2-methoxy-7,8-dihydronaphthalene. The vinylsilane 7 was similarly converted in 71% yield to the corresponding dione 16, mp 123-127°.

The cases described above all represent the use of a vinylsilane chain as a cyclohexenone precursor. The method can, however, be used in other cases as well. For instance, the vinylsilane 17 (formed from the appropriate allylic iodide and 3) gave after 29 hr at room temperature with m-chloroperbenzoic acid 60% yield of the aldehyde 18, oxidized by Jones reagent to the corresponding keto acid.13 Finally, the application to a cyclopentenone is illustrated by the conversion of the vinylsilane 19 (from 3 and the appropriate iodide).

In that case, the peracid treatment led not to the dione but, in agreement with the postulate of ketone participation, to the cyclic ketal 20 (quantitative yield). This, in keeping with the greater difficulty of eliminating the primary oxygen function, required refluxing with 20% sulfuric acid-methanol for quantitative conversion to the related dione 21, cyclized (reflux with 1 M potassium hydroxide-methanol for 10 hr) in 83% yield to the known 14 methylhydrindenone (22).15

(15) We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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Received February 19, 1974

Synthetic Routes to Halomethyl Vinylsilanes

Sir:

The demonstration that the vinylsilane system can be used as a relatively unreactive masked carbonyl via