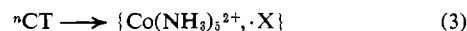


Figure 1. Absorption spectrum (upper curve) and quantum yields of Co^{2+} (lower curves) from ultraviolet irradiations of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. For lower set of curves quantum yields were obtained in water (solid circles) or 50% glycerol-water (open circles) solutions; activation 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 $\lambda > 450$ 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.²⁷ 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^{2,22}) and population of a reactive charge transfer excited state. It is most significant that for this complex the decreased values of $\phi_{\text{Co}^{2+}}$ 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 Co^{2+} which we have

(27) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Wiley, New York, N. Y., 1961.

obtained for high energy irradiations in glycerol water media may arise from either or both of two plausible mechanisms:²⁸ (1) there may be a relatively low energy onset²⁹ of a CTTM state corresponding to photo-oxidation of solvent glycerol³⁰ 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 (${}^1\text{CT}^*$) reached in the initial excitation must have ground state (${}^1\text{A}$) solvation, and this solvent environment must ultimately relax to solvation appropriate to the radical pair products ($\{\text{Co}(\text{NH}_3)_5^{2+}, \cdot\text{X}\}$); eq 1–3 describe the proposed



sequence of events, where the excited state ${}^n\text{CT}$ could in principle differ from ${}^1\text{CT}^*$ in thermal equilibration and also in spin multiplicity.³¹ 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 suspected³² 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 (${}^1\text{CT}^*$, ${}^n\text{CT}$, or other states populated along the coordinate for reaction 2).

(28) Possible variations in the type of radical pair species (geminate or secondary or singlet, triplet, or quintet) seem less plausible and will be discussed in detail elsewhere.

(29) That is the lowest energy manifestation of "solvent" oxidation would have to occur at about 285 nm for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ and at about 240 nm for $\text{Co}(\text{NH}_3)_5^{2+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{N}_3$).

(30) When glycerol oxidation has been observed, we have no means of determining unequivocally whether glycerol oxidation occurred in a primary photoredox step or in subsequent reactions of primary radicals. It is also to be noted that we prepared our glycerol solutions from reagent grade glycerol which was found to be nearly nonabsorbing at $\lambda \geq 214$ nm (absorbance of neat glycerol at 214 nm ≤ 0.1).

(31) Note that the spin of a $\{\text{Co}(\text{NH}_3)_5^{2+}, \cdot\text{X}\}$ radical pair containing a high spin (i.e., ground state) $\text{Co}(\text{NH}_3)_5^{2+}$ species does not correlate with a singlet CTTM state.

(32) However, analogous involvements of solvent in the photophysics of charge transfer complexes have been proposed, see M. Ottolenghi, *Accounts Chem. Res.*, 6, 153 (1973).

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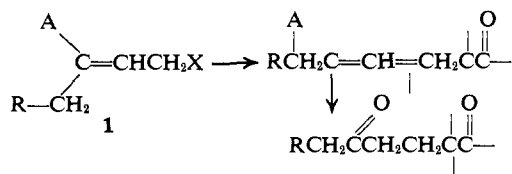
Received October 23, 1973

Vinylsilanes as Carbonyl Precursors. Use in Annelation Reactions

Sir:

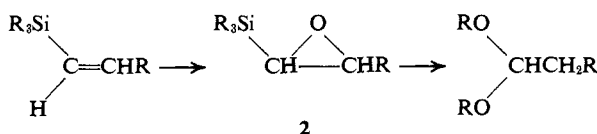
The addition of a 3-ketoalkyl chain α to a carbonyl function, an important step in annelation reactions, requires either Michael addition to a suitable vinyl ketone or alkylation with a 3-ketoalkyl halide equivalent. The latter process is in principle the more general. Maximum versatility, including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

cally generated enolates, requires that the halide be especially reactive, e.g., a benzylic or allylic halide. The isoxazole annelation sequence¹ belongs to the benzylic type halide, while suitable allylic halides have to be of type **1** in which the substituted vinyl system A—



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

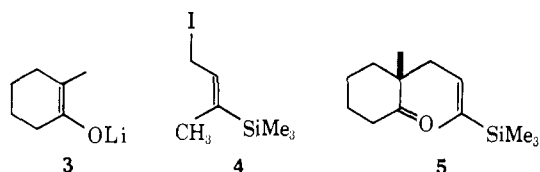
We have previously shown that epoxysilanes such as **2** are converted into acetals by refluxing with methanolic



sulfuric acid,² thus demonstrating the potential of the vinylsilane function as a latent carbonyl.

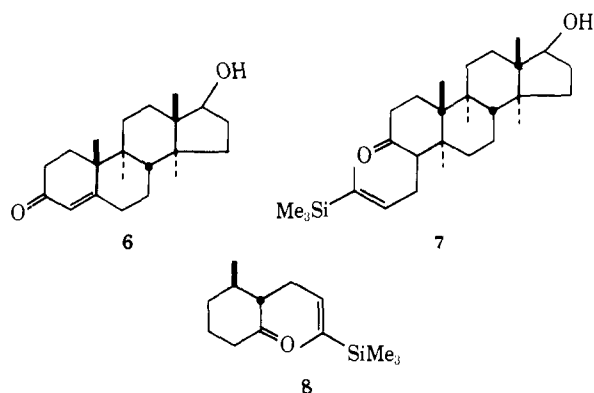
We now describe the extension of this concept to annelation reactions. We first demonstrate the suitability of the silylallyl halides in various types of alkylation reactions and then show that the alkylated products can be transformed *under unusually mild conditions* into the 1,5- and 1,4-diketone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

Alkylation of the lithium enolate **3**, kinetically gen-



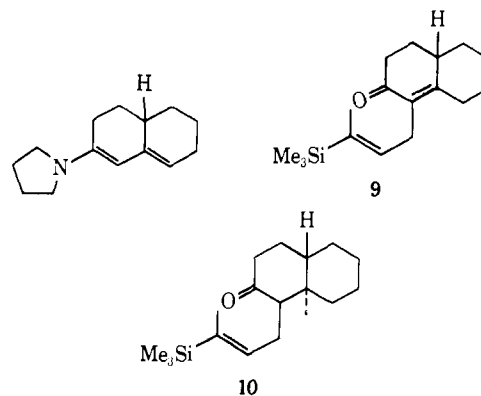
erated from its enol acetate,³ took place readily with 1 equiv of the iodide **4**⁴ (tetrahydrofuran, room temperature) to give **5** (91% yield): bp 45° (0.02 mm); nmr (CCl₄) δ 5.51 (1h, t, *J* = 7 Hz, of q, *J* = 1.5 Hz, HC=C), 0.98 (3 H, s, CH₃), 0.00 (9 H, s, CH₃Si); mass spectrum *m/e* 238, 223, 112, 73.⁵

The synthetically very important trapping of enolates regiospecifically produced by lithium reduction of enones⁶ 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 (additional lithium was added if necessary until a light blue color persisted) was followed by a solution of 2 equiv of the iodide **4** in ether. Evaporation after 2 hr at -33° gave the alkylated steroid **7**



(silica gel chromatography 80:20, ether:hexane), mp 151–152° in 58% yield. Enolates regiospecifically produced by conjugate alkyl cuprate addition are also efficiently trapped⁷ by the silyl reagents. Addition of cyclohexenone to 1 equiv of lithium dimethyl cuprate in ether followed by 1 equiv of the iodide in tetrahydrofuran (final ratio tetrahydrofuran:ether 2:1) gave after 5 hr at room temperature, the alkylated cyclohexenone **8** in 75% yield after silica gel chromatography (60:40, hexane:methylene chloride). The structure follows from its conversion to the methyl octalone **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 Δ^{1,9}-2-octalone⁸ 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.² We also found that similar conditions were required for the transformation of the simple epoxysilane **11** (made by chloroplatinic acid-catalyzed addition of triethylsilane⁹ to 4-octyne, followed by *m*-chloroperbenzoic acid in methylene chloride) to 4-octanone. It is especially worth noting that **11** was

(7) For the trapping of enolates from cuprate addition, see G. Stork, *Pure Appl. Chem.*, **17**, 1383 (1968).

(8) Cf. L. Velluz, G. Nominé, J. Mathieu, D. Bertin, J. Tessier, and A. Pierdot, *C. R. Acad. Sci.*, **250**, 1084 (1960).

(9) Cf. E. Y. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements," Consultants Bureau, New York, N. Y., 1966.

(1) 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).

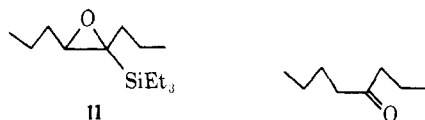
(2) G. Stork and E. Colvin, *J. Amer. Chem. Soc.*, **93**, 2080 (1971).

(3) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963); H. O. House, M. Gall, and H. D. Olmstead, *ibid.*, **36**, 2361 (1971).

(4) The synthesis of the silylated allyl 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**, 3684 (1974).

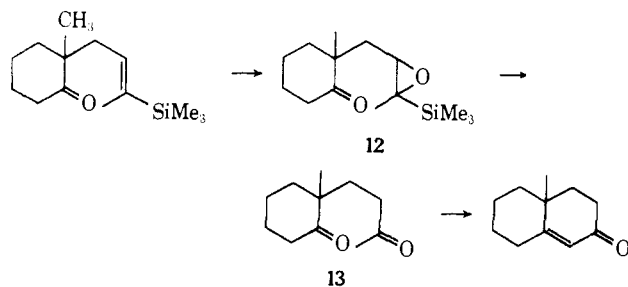
(5) Satisfactory nmr, ir, and mass spectral data were obtained for all new compounds reported. Chloroform (δ 7.24) was used as an internal standard for the nmr spectra of compounds containing the trimethylsilyl group.

(6) G. Stork, P. Rosen, N. L. Goldman, R. V. Coombs, and J. Tsuji, *J. Amer. Chem. Soc.*, **87**, 275 (1965).



unaffected by formic acid at room temperature or by heating with acetic acid in ethanol.

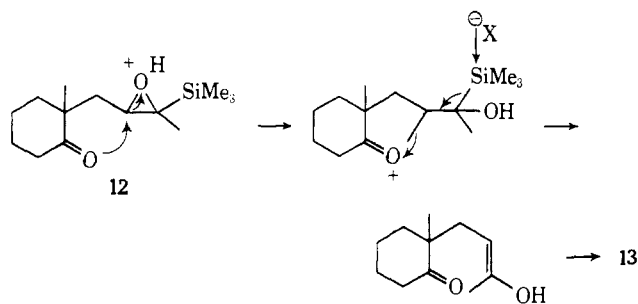
In startling contrast, while treatment of the ketonic vinylsilane **5** in methylene chloride with a slight excess of *m*-chloroperbenzoic acid at 0° for 10 min gives largely the epoxysilane **12**, further keeping of the re-



action 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*-chlorobenzoic 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 (*vide 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.

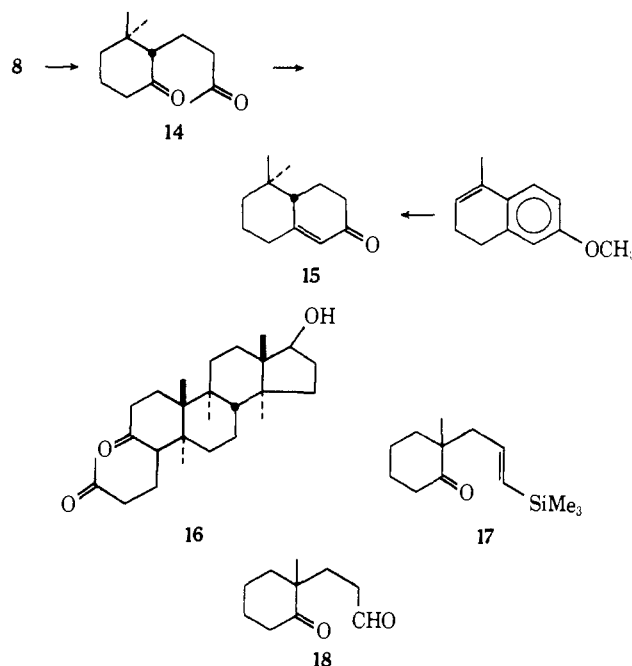


Under similar conditions, the vinylsilane **8** was transformed (final treatment with formic acid) to the dione **14** (83% yield), further cyclized in 82% yield (3 *M* potassium hydroxide in ethanol) to 5-methyl- $\Delta^{1,9}$ -2-octalone (**15**) identical with an authentic sample made by Birch reduction of the known¹² 5-methyl-2-methoxy-7,8-dihydronaphthalene. The vinylsilane **7** was similarly converted in 71% yield to the corresponding dione **16**, mp 123–127°.

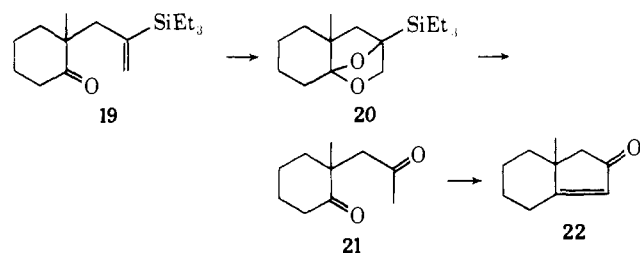
The cases described above all represent the use of a vinylsilane chain as a cyclohexenone precursor. The

(10) J. A. Marshall and D. J. Schaeffer, *J. Org. Chem.*, **30**, 3642 (1965).
 (11) G. Stork and R. Borch, *J. Amer. Chem. Soc.*, **86**, 935 (1964).
 See also Y. Gaoni, *J. Chem. Soc.*, 2925, 2934 (1968).

(12) G. Stork, A. Meisels, and J. E. Davies, *J. Amer. Chem. Soc.*, **85**, 3419 (1963).



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 known¹⁴ methylhydrindenone (**22**).¹⁵

(13) R. L. Frank and R. C. Pierle, *J. Amer. Chem. Soc.*, **73**, 724 (1951).

(14) R. Fraisse-Jullien and C. Frejaville, *Bull. Soc. Chim. Fr.*, 4449 (1968).

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

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Synthetic Routes to Halomethyl Vinylsilanes

Sir:

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